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(56) Documents cited GB 1481472 GB 1463429 GB 1399257 GB 1387356 GB 1344918 GB 1342278 GB 1323728 GB 1283663
(58) Field of search C3B C3P

(71) Applicants Minnesota Mining and Manufacturing Company, 3M Center, Saint Paul, Minnesota 55101, United States of America
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(74) Agents Lloyd Wise, Bouly & Haig

(54) **Shaped plastic articles having replicated microstructure surfaces**

(57) An article comprising a shaped, plastic layer or body comprising crosslinked polymer with hard and soft segments or moieties and having a microstructure-bearing surface is prepared by a process comprising filling a mold master, bearing or encoded with the microstructure to be replicated, with a fluid, castable, one-part, preferably solvent-free, radiation addition-polymerizable, crosslinkable, synthetic, organic oligomeric composition (or precursors thereof) having "hard" segments and "soft" segments, exposing the resulting cast composition to radiation, preferably actinic radiation such as ultraviolet radiation, and thereby forming said article, e.g., a retro-reflective cube-corner sheeting, Fresnel lens or video disc.

Certain of the chemical formulae appearing in the printed specification were submitted in formal form after the date of filing.

GB 2 027 441 A

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/GB 96/03016

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0057271 A	11-08-82	AT 9851 T	15-10-84
		JP 1369990 C	25-03-87
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EP 0715189 A	05-06-96	FR 2726660 A	10-05-96
		JP 8211216 A	20-08-96
DE 4225007 A	03-02-94	NONE	

INTERNATIONAL SEARCH REPORT

Int. ional Application No
PCT/GB 96/03016

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JOURNAL OF PHYSICS E SCIENTIFIC INSTRUMENTS., vol. 3, no. 12, December 1970, BRISTOL GB, pages 953-961, XP002027792 LOEWEN E G: "Diffraction Gratings for Spectroscopy" see the whole document	24
A	JOURNAL OF VACUUM SCIENCE AND TECHNOLOGY: PART B, vol. 5, no. 1, January 1987, NEW YORK US, pages 33-36, XP002027793 TERUHIRO SHIONO ET AL: "Computer controlled electron beam writing system for thin film micro optics" see the whole document	29
A	SENSORS AND ACTUATORS A, vol. A51, no. 1, 1 October 1995, pages 77-80, XP000545377 KLUMPP A ET AL: "ANISOTROPIC ETCHING FOR OPTICAL GRATINGS" see the whole document	29

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 96/03016

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 G02B5/18 B42D15/10 G06K19/16

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 G02B B42D G06K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 057 271 A (LANDIS & GYR AG) 11 August 1982	1,3,5, 20,23
A	see page 20, line 8 - line 15	6,7,9, 10,16, 18,21, 24,29
	see figure 32	

P,X	EP 0 715 189 A (FRANCE TELECOM) 5 June 1996	1,3-5,16
P,A	see the whole document	6,7,9, 10,18,21

A	DE 42 25 007 A (MUELLER HELMUT FRANK OTTOMAR P) 3 February 1994 see the whole document	1,6,11

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
18 March 1997	26.03.97

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016	Ward, S

Form PCT/ISA/210 (second sheet) (July 1992)

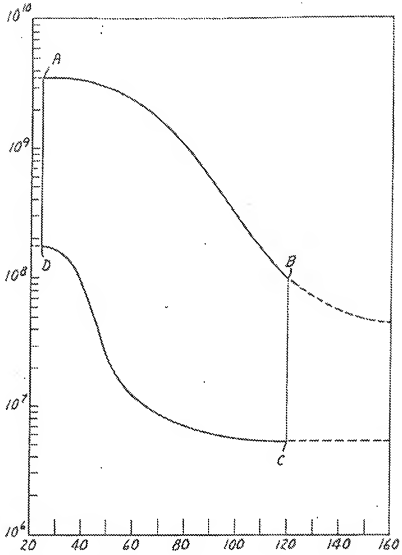

FIG. 1

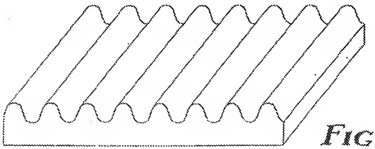

FIG. 2

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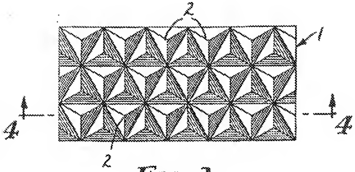

FIG.3

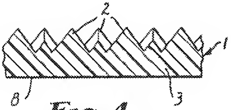

FIG. 4

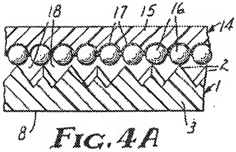

FIG.4A

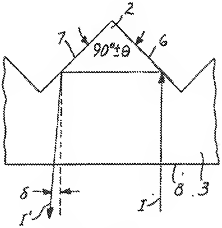

FIG. 5

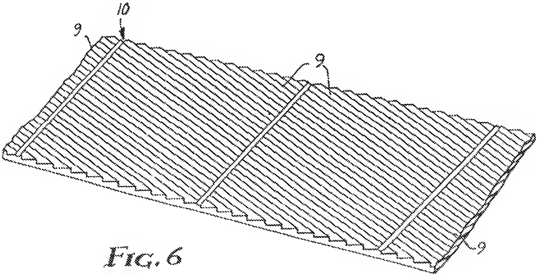

FIG. 6

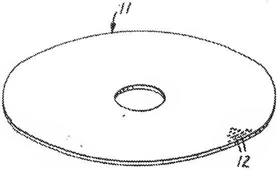

FIG. 7

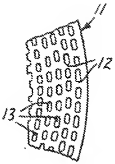

FIG. 8

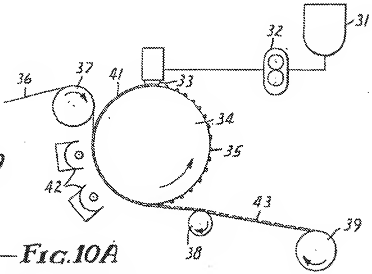

FIG. 9

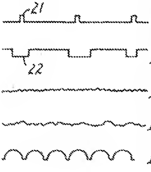

FIG.10A
FIG.10B
FIG.10C
FIG.10D
FIG.10E
FIG.10F

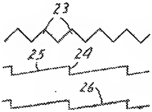

FIG.10G
FIG.10H
FIG.10I

SPECIFICATION

Shaped plastic articles having replicated microstructure surfaces

This invention relates to the replication of surface bearing microstructure. In another aspect it relates to shaped plastic articles, such as retroreflecting cube-corner sheeting, Fresnel lens elements, diffraction gratings, video discs, and ophthalmic lenses, having replicated microstructure-bearing surfaces, and to a process for the preparation of the articles. In another aspect, it relates to novel castable radiation curable oligomers, a process for their preparation, and the use of such material in making said replicated plastic articles.

Many materials, techniques and processes have been proposed, patented or used for replicating various microstructure-bearing surfaces in the form of embossed, cast or molded plastic articles, e.g., see J. of Applied Physics, Vol. 45, No. 10, p. 4557, October, 1974. Some of these have been of practical value though of limited application in many instances while others have been found wanting as impractical, especially where the object has been high fidelity and durability of replication or mass production capability. In many cases, the progress in this art has been stymied by lack of suitable replicating materials.

For example, in the area of retroreflective cube-corner sheetings, used as traffic signs and the other applications where light reflection is used for traffic direction and safety, U.S. Pat. No. 3,689,346 (Rowland) discloses a process for the continuous replication of such articles by depositing a crosslinkable, partially polymerised resin, such as certain acrylic acid ester resins, on a negative molding surface to be replicated, and exposing the resin to actinic light or heat to solidify the resin. The resins used typically exhibited relatively high levels of shrinkage upon solidifying or curing, thus giving rise to optical imperfections in the cube-corner microstructure, that is, changes in the angles between the faces of the cube-corner which produce light scattering rather than the desired maximum retroreflectivity. Attempts to overcome shortcomings are described in U.S. Pat. No. 3,935,359 (Rowland) which discloses filling further resin in the void resulting from the shrinkage, and U.S. Pat. No. 3,980,393 (Heasley et al) which discloses using a lens system in conjunction with the cube-corner structure in order to compensate for the shrinkage. Such modifications are, of course, costly and demonstrate a need for replicating materials which do not significantly shrink and so cause optical imperfections in the replication.

An example where plastics have been used in replication of optical surfaces or elements is U.S. Pat. No. 3,931,373 (Beattie) which discloses replicating ophthalmic lenses from plastic compositions, such as methyl methacrylate, by use of a replicating mold made of certain polymeric materials, such as certain copolymers of styrene and methyl methacrylate, to prevent distortion of lenses during cure. French Pat. No. 2,247,329 discloses making replicas of video discs using ultra-violet radiation curable acrylics and epoxies. U.S. Pat. No. 3,334,958 (Appledorn) discloses Fresnel lens elements stamped from polymerized methyl methacrylate using molds made from machined master lenses.

Other U.S. patents disclosing replication of various articles using plastic compositions are U.S. Pat. Nos. 2,310,790 (Jungerson), 2,482,598 (Roos), 3,565,978 (Folger et al), 3,190,947 (Norcros), 3,369,949 (Forrest) 3,667,946 (Sturdevant), 2,524,862 (White); the replication process of these patents require high molding temperatures or pressures which cause loss of fidelity in the replicated structure, use of solvents which require a long time to evaportate, long cure cycles, curable materials which have a limited "pot" life, or result in replicated articles having limited toughness and dimensional stability and with severe shrinkage.

Though oligomers or cured polymers with "hard" and "soft" segments or blocks have been disclosed in the prior art, e.g., see "Block Copolymers", Allport and Janes, published by Wiley & Son, N.E. Chap. 8C, (1973), "Polymer Blends & Copolymers", Manson & Sperling, published by Plenum Press, N.Y., p. 153—166, (1976), "Polymer Engineering & Science", Vol. 11, No. 4, p. 369, (1971), "Encyclopedia of Polymer Science & Technology", Kirk-Othmer, Suppl., Vol. 1, p. 521—543 (1976, and U.S. Pat. Nos. 3,560,417 (Pizzi et al) and 4,077,932 (Columbus), those materials have not been disclosed as useful in making shaped plastic articles comprising crosslinked polymer and having replicated microstructure surfaces.

Briefly, in one aspect, this invention provides an article comprising a shaped, plastic, monolithic layer (or body) comprising certain crosslinked polymer and having one or more, like or different, replicated microstructure-bearing surfaces. An example of such article is a traffic control sign comprising a layer in the form of a self-supporting or free film or sheet of said crosslinked polymer and having on one side a microstructure-bearing surface in the form of a replicated array of retroreflective cube-corners, the side of which sheet can be a replicated "flat" surface. Such articles are prepared by a process comprising filling a mold master, bearing the microstructure to be replicated, with a fluid, castable, one-part, preferably solvent-free, radiation addition-polymerizable, crosslinkable, oligomeric composition (or precursors thereof) having both "hard" and "soft" segments, exposing the resulting cast composition to radiation, preferably actinic radiation such as ultraviolet radiation, and thereby forming said article. Said process lends itself to rapid, mass production of such articles with no adverse environmental impact because no or only a minor amount of solvent or other volatiles are evolved and it can be carried out at ambient temperatures and pressures. The process also lends itself to replication of

articles with microstructure comprising utilitarian discontinuities, such as projections and depressions, which are readily released from the mold master without loss of the detail of the master and with retention of the replication of such detail under a wide variety of conditions during use. The articles can be formed with a wide variety of desired properties, such as toughness, flexibility, optical clarity or homogenity, and resistance to common solvents, the microstructure of such articles having high thermal dimensional stability, resistance to abrasion and impact, and integrity even when the articles are bent, e.g., 180°. The physical properties of the crosslinked polymer can be varied by proper selection of the oligomeric composition. The tensile strengths of the polymer can be varied from 70 to 700 kg/cm^2, the modulus of elasticity can be varied from 140 to 14000 kg/cm^2, and the elongation-to-break can be varied from 5 to 300%. The optical homogenity of the polymer is manifested by at least 91% transmission of light, haze of less than 5%, and birefringence, Δn, of less than 0.002, and the flexibility is manifested by desirable dynamic shear moduli over a wide temperature range, e.g., 23 to 120°C.

FIG. 1 is a plot of the dynamic shear moduli of illustrative plastics used in making plastic articles of this invention; FIG. 2 is an isometric view of replicated diffraction gratings of this invention; FIG. 3 is a plan view of replicated array of cube-corner retroreflective elements of this invention; FIG. 4 is an elevation section of FIG. 3 taken along 4—4; FIG. 4A is an elevation section of a modified retroreflective sheeting employing the array of FIG. 4; FIG. 5 is a diagrammatic view of a cube-corner element; FIG. 6 is an isometric view of a sheet of replicated linear Fresnel lenses of this invention; FIG. 7 is an isometric view of a replicated video disc of this invention; FIG. 8 is an enlarged view of a portion of FIG. 7; FIG. 9 is a schematic diagram of apparatus useful in making a sheet of cube-corner elements of FIGS, 3 and 4; and FIGS. 10A—10I are diagrams of illustrative profiles of various replicated microstructures of this invention.

The term "microstructure", used herein the context of a shaped article having a surface bearing microstructure, means the configuration of a surface which depicts or characterizes the predetermined desired utilitarian purpose or function of said article. Discontinuities, such as projections and indentations, in the surface will deviate in profile from the average or center line drawn through the microstructure such that the sum of the areas embraced by the surface profile above the line is equal to the sum of those areas below the line, said line being essentially parallel to the normal surface (bearing the mocrostructure) of the article. The heights of said deviations will be ± 0.005 μm to ± 750 μm through a representative characteristic length of the surface, e.g., 1 to 30 cm. Said average profile, or center line, can be plano, concave, convex, aspheric or combinations thereof. Articles where said deviations are of low order, e.g. from ± 0.005 μm to 0.1 μm or, preferably, to ± 0.05 μm, and said deviation are of infrequent or minimal occurance, i.e., the surface is free of any significant discontinuities, are those where the microstructure-bearing surface is an essentially "flat" or "perfectly smooth" surface, such articles being useful, for example, as precision optical elements or elements with a precision optical interface, such as ophthalmic lenses. Articles where said deviations are of said low order and of frequent occurrence are those, for example, bearing utilitarian discontinuities, as in the case of articles having anti-reflective microstructure. Articles where said deviations are of high order, e.g., from ± 0.1 μm to ± 750 μm, and attributable to microstructure comprising a plurality of utilitarian discontinuities which are the same or different and spaced apart or contiguous in a random or ordered manner, are articles such as retroreflective-cube-corner sheeting, linear Fresnel lenses, and video discs. The microstructure-bearing surface can contain utilitarian discontinuities of both said low and high orders. The microstructure-bearing surface may contain extraneous or non-utilitarian discontinuities so long as the amounts or types thereof do not significantly interfere with or adversely affect the predetermined desired utilities of said articles. It may be necessary or desirable to select a particular oligomeric composition whose shrinkage upon curing does not result in said interfering extraneous discontinuities, e.g., a composition which shrinks only 2 to 6%.

The above described profiles and the dimensions and spacing of said discontinuities are those discernible by an electron microscope at 1000X to 100,000X or an optical microscope at 10X to 1000X.

In FIGS. 10A—10I, various illustrative profiles of replicated microstructure-bearing surfaces are shown. The profile of FIG. 10A is plano, free of utilitarian discontinuities, and is illustrative of the microstructure of an ophthalmic lens or optical flat. The profiles of FIGS. 10B and 10C have spaced-apart utilitarian discontinuities which in FIG. 10B are in the form of projection or raised areas 21 and in FIG. 10C are in the form of depressions or indentations 22, such profiles being illustrative, for example, of microstructure present on video discs. FIGS. 10D and 10E depict profiles with a plurality of contiguous, utilitarian discontinuities, such profiles being illustrative, for example, of species of anti-reflective surfaces. FIG. 10F depicts a profile with a plurality of closely spaced arcs, e.g., hemispherical, and is illustrative of microstructive in the form of utilitarian lenslets, e.g., a replicated beaded layer which can be vapor coated with specular light reflecting material to provide a retroreflective sheet. FIG. 10G depicts a profile with individual contiguous utilitarian discontinuities in the form of projections 23 of like size and shape, and is illustrative of cube-corner retroreflective microstructure made up of trihedral prism elements. FIG. 10H depicts a profile with utilitarian discontinuities in the form of alternating steps 24 and lands 25, such a profile being illustrative of a linear Fresnel lens. And FIG. 10I depicts a profile which is a combination of the types illustrated in FIGS. 10C and 10H, the lands 26

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being "rough" due to low order utilitarian discontinuities, such a profile being illustrative of a linear Fresnel lens with anti-reflective microstructure.

Radiation addition-polymerizable, crosslinkable oligomeric compositions useful in making said shaped articles of this invention comprise radiation addition-polymerizable, oligomers or prepolymers having (1) one or more like or different "hard" (rigid) segments ("H"), viz., mono- or poly- and preferably di-valent moieties containing one or more carbocyclic and/or heterocyclic groups are preferably difunctional linking groups with hydrogen bonding capabilities, e.g., carbonyldioxy, —OC(O)O—, carbamato, —NHC(O)O—, ureylene, —NHCONH—, amido, —NHCO—, and oxy, —O—, said moieties, when their valences are satisfied by protons, having at least one major transition temperature above 250°K, preferably above 350°K, said transition being a glass transition temperature or crystalline melting point, such as are usually detected by differential thermal analysis or thermomechanical analysis, (2) one or more like or different "soft" (flexible) segments ("S"), viz., mono- or, preferably, poly-valent moieties, such as a polyester, polysiloxane, polyacrylate, polyether or polyolefin segment, each of which has a number average molecular weight in the range of about 500 to 5000 and each of which in the form of homopolymer has a glass transition temperature below 250°K, and (3) one or more like or different monovalent moieties ("E") containing a radiation sensitive, addition-polymerizable, functional group such as acrylyl, methacrylyl, allyl or vic-epoxy group. The amount of "H", "S" and "E" segments or moieties in said oligomeric composition are such that the radiation-cured crosslinked plastic derived therefrom preferably has dynamic shear moduli, over the temperature range of 23° to 123°C, on or within the boundary of area A—B—C—D of FIG. 1. Where the oligomers contain two or more "H" segments, such segments can be the same or different, as is true of the "S" segments and the "E" moieties. Further, the oligomers are free of labile groups, viz., —O—O— and —N=N—, and generally will have a number average molecular weight of about 1000 to 30,000 grams per mole.

A class of such oligomers can be represented by the general formula

$$\left[\text{"E"}(\text{"H"})_{\alpha}\left[\text{"S"}(\text{"H"})_{\alpha}\right]_{\beta}\right]_{\gamma}\text{"S"} \qquad \text{I}$$

where "E", "H", and "S" are as broadly defined above, α is 1 or 2, β is zero or an integer up to 20 whose average is less than about 5, and γ is 2 or 3.

"E" in formula I can be represented by the formula

$$CH_2{=}\overset{R^1}{\overset{|}{C}}-(\overset{O}{\overset{\|}{C}})_a-(A)_b-\left[(CH_2)_e\right]_c-(A)_d \qquad \text{II}$$

where R^1 is a hydrogen atom or methyl,
each A is independently —NH— or —O—,
a, b, c and d are each independently zero or 1, with the provisos that
(1) at least one of b and d must be 1,
(2) if b and c are both zero, then a and d must be 1,
(3) if b and d are both 1, then a and c must be 1, and e is at least 2, and
(4) if d is 1 and a and b are both zero, then c must be 1,
e is an integer of 1 to 5,

subgenera of formula II being these of the formulas:

$$CH_2{=}\overset{R^1}{\overset{|}{C}}-\overset{O}{\overset{\|}{C}}-A-, \qquad \text{IIA}$$

where preferably R^1 is methyl and A is —O—,

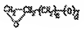
$$CH_2{=}\overset{R^1}{\overset{|}{C}}-\overset{O}{\overset{\|}{C}}-O-(CH_2)_e-A-. \qquad \text{IIB}$$

where preferably R^1 is methyl, A is —O—, and e is 2,

and

$$CH_2{=}\overset{R^1}{\overset{|}{C}}-CH_2-A- \qquad \text{IIC}$$

where preferably R^1 is a hydrogen atom and A is —O—.
"E" in formula I can also be that represented by the formulas: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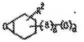
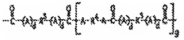

IV

where (in formulas III and IV)
R^2 is hydrogen or a lower alkyl (e.g., with 1 to 4 carbon atoms and preferably is methyl),

B is $-(CH_2)_f-$, $-CO-$, $-(CH_2)_fCO-$ or

$-(CH_2)_fOC(O)-(CH_2)_fC(O)O(CH_2)_f$,

and each f is an integer of 2 to 5, each d is independently zero or 1, and e is 1 to 5.
"H" in formula I can be represented by the formulas: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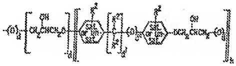
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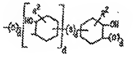
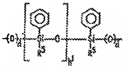
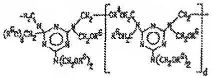

VII

and

and 
VIII

or, where "E" in formula I is selected from the group of structures represented by formulas IIA, IIB, and IIC, "H" can be represented by the following structure:


IX

where (in formulas V, VI, VII, VIII and IX),
each R^2 is independently as defined above for formula IV,
each R^3 is independently a di-valent carbocyclic-containing radical derived from benzene, napthalene, cyclohexane, dicyclohexylmethane, diphenylmethane, or norbornene, and their lower alkyl-substituted derivatives, by removal of two of their hydrogen atoms,
each R^4 is independently an alkylene moiety with 2 to 10 (and preferably 2, 4 or 6) carbon atoms, or a cycloalkylene moiety with 6 to 10 carbon atoms (and preferably 8 carbon atoms, 6 of which are ring-carbon atoms),
each R^5 is independently a phenyl moiety or (preferably) methyl,

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each R^6 is independently a lower alkyl with 1 to 4 carbon atoms, preferably methyl,
g is zero or a number up to 5 (and preferably an average of 1 to 3),
B is as defined in formula IV,
h is an integer of 1 to 10,
h' is zero or an integer of 1 to 10, each d, d' and d'' is independently zero or 1, with the proviso that if either one of d' or d'' is 1, then the other is zero, and
A is as defined above for formula II.

"S" in formula I can be the polyether (or polyoxyalkylene), polyester, polyolefin, polyacrylate, or polysiloxane residue remaining after removal of the active hydrogen atoms of polyols (illustrated by the generic formula $R_3(OH)$ hereinafter), such as polyether (or polyoxyalkylene) polyols, polyester polyols, polyether polyester polyols, polyolefin polyols, polysiloxane polyols, and poly(alkylacylate) polyols, or polyamines (illustrated by the generic formula $R_3(NH_2)y$ hereinafter) such as polyoxalkylene polyamines, polyolefin polyamines, and polysiloxane polyamines, said polyoxyalkylene residue including those of the formula:

$$\left[A-R^7-(OR^7)_i-O\right]_j-(R^8)_d-(R^7-A)_c \qquad X$$

where each A is independently —NH— or —O—,
$(OR^7)_i$ is oxyalkylene or poly(oxyalkylene),
R^7 is an alkylene of 2 to 4 carbon atoms, such as

$$-(CH_2)_2-,\ -(CH_2)_3-,\ -(CH_2)_4-,\ -CH_2CH(CH_3)-,$$

$$-CH_2CH(CH_3)CH_2-, \text{ and } -CH(CH_3)CH(CH_3)-,$$

R^8 is a saturated aliphatic radical free of active hydrogen atoms and which can contain 1 or 2 nonvicinal catenary oxygen or nitrogen atoms, R^8 having a valence equal to j and 2 to 10 carbon atoms
i is a number of 1 to 20, preferably 2 to 10, and
j is an integer of 1 to 3, and
d and c are each independently zero or 1 with the provisos that when d is 1, then c is zero and j is 2 or 3, and when d is zero, then j is 1,

subgenera of "S" within the scope of formula X being those polyoxyalkylene residues represented by the general formulas:

$$-A-(CH_2)_{f'}-\left[O-(CH_2)_{f'}\right]_{i'}-O-(CH_2)_{f'}-A- \qquad XA$$

where preferably each f' is independently 3 to 5 (more preferably 4) and i' is 5 to 10,

$$\left[A-(CH_2)_{f'}-\left[O-(CH_2)_{f'}\right]_{i'}-O\right]_k-R^8 \qquad XB$$

where preferably f' is 3 to 5 (more preferably 4), i' is 5 to 10, and k is 2 or 3 and the valence of R^8,

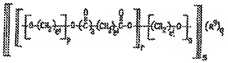
$$-A-(CH_2)_2-\left[\left[O-(CH_2)_2\right]_m-\left[O-CH_2\overset{CH_3}{\overset{|}{C}H}\right]_n\right]-A- \qquad XC$$

where the groups enclosed by the single brackets with subscripts m and n are repeating units randomly distributed, m is zero or 1 to 4, n is 4 to 20, with the proviso that n/m is at least 4,

$$\text{and} \quad \left[A-R^7-\left[\left[O-(CH_2)_2\right]_m-\left[O-CH_2\overset{CH_3}{\overset{|}{C}H}\right]_n\right]-O-\right]_k-R^8 \qquad XD$$

where the groups enclosed by the brackets with subscripts m and n are repeating units randomly distributed within the double brackets, m, n, and n/m are as defined for formula XC and k is 2 or 3 and is the valence of R^8,

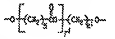
or "S" in formula I is a said polyester residue represented by the formula:



XI.

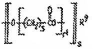
where R^9 is a saturated aliphatic radical free of active hydrogen atoms and can contain 1 or 2 non-vicinal catenary oxygen or nitrogen atoms, R^9 having a valence equal to s and 2 to 10 carbon atoms,
each a, o, p and q is independently zero or 1,
each a' is independantly an integer of 2 to 10, preferably 2 to 5,
each r is independently a number of 1 to 20, preferably 1 to 10, and
each s is independently an integer of 1 to 3 with proviso that
when q is 1, then s is 2 or 3 and o is zero and either a and p ar both zero or both 1, and
when q is zero, then s and o are 1 and either a and p are both zero or both 1,

subgenera of "S" within the scope of formula XI being those polyester residues (viz., polycaprolactone residues) represented by the general formulas:



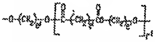
XIA

where r' is a number of 1 to 10 and a' is 2 or 3,



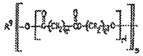
XIB

where r' is a number of 1 to 10 and s is 2 or 3, and R^9 is preferably oxyalkylene, e.g., $-CH_2CH_2OCH_2CH_2-$, polyoxyalkylene, or alkanetriyl, e.g., $(-CH_2)_3CCH_2CH_3$,



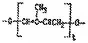
XIC

where each a' is independently a number of 2 to 5 and r' is a number of 1 to 10,

and 

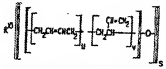
XID

where a' is a number of 2 to 5, r' is a number of 1 to 10, R^9 is as defined for formula XIB, and s is 2 or 3, or "S" in formula I is a said polyolefin residue represented by the formulas:



XII

where t is a number of 7 to 35,

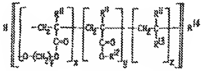
and 

XIII

where the group enclosed by the single brackets with the subscripts u and v are repeating units randomly distributed within the double brackets and u and v are integers whose sum is from 2 to

20 and u/v is a ratio of 1/4 to 4/1, s is 2 or 3, and R^{10} is polyvalent carbocyclic-containing radical derived from benzene, naphthalene, or a phenyl-substituted benzene by removal of 2 or more hydrogen atoms,

or "S" in formula I is a said polyacrylate residue represented by the formula:

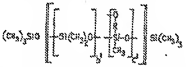


XIV

where each
R^{11} is independently hydrogen or methyl,
R^{12} is independently an alkyl of 2 to 10 carbon atoms, preferably butyl;
R^{13} is independently —C(O)OCH$_3$, —CN or phenyl,
R^{14} is —SRH, —SR^{15}O—, —SCH$_2$C(O)OR^{15}H or H, where R^{15} is an alkylene having 1 to 12 preferably 2, carbon atoms,
f is an integer of 2 to 5
the groups enclosed by the single brackets with subscripts x, y and z are repeating units randomly distributed within the double brackets, the sum of x, y and z being such that the number average molecular weight of the totality of said repeating units is about 500 to 5000, the units enclosed by brackets with subscripts x and y always being present and the units enclosed by the bracket with subscript z being optionally present,
or "S" in formula I is a said polysiloxane residue represented by the formulas:

$$-O-R-\left[Si(CH_3)_2-O\right]_{b'}-R-O- \qquad XV$$

where b' is a number of 6 to 35, and R is a linear or branched alkylene group having 1 to 12 carbon atoms or a polyoxyalkylene group having 4 to 80 carbon atoms and 1 to 40 oxygen atoms,

and  XVI

where the groups enclosed by the single brackets with subscripts b' and c' are repeating units randomly distributed within the double bracket, b' being a number of 6 to 35 and c' being 2 or 3, and R is as defined above for formula XV.

Representative species of oligomers useful in making the shaped articles of this invention and falling within the scope of formula I include those having the structures represented in Table I.

TABLE I

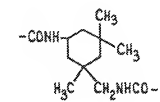
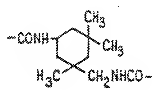
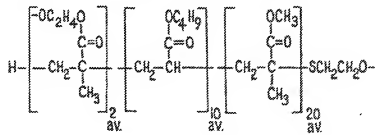
FORMULA No.	"E"	"H"	"S"
XVII	$CH_2{=}C(CH_3)COOC_2H_4O$		$\left[\left[-O-(CH_2)_5-CO-\right]_{1.86\ av.}-OC_2H_4-\right]_2 O$
XVIII	ditto	ditto	$\left[\left[-O-(CH_2)_4-\right]_{8.5\ av.}-OC_2H_4-\right]_2 O$
XIX	$CH_2{=}C(CH_3)COOC_2H_4O-$		$\left[\left[-O-(CH_2)_5-CO-\right]_{5\ av.}-OC_2H_4-\right]_2 O$
XX	ditto	ditto	

TABLE I – cont'd

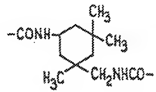
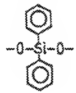
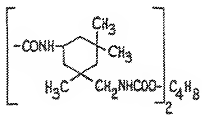
FORMULA No.	"E"	"H"	"S"
XXI	$CH_2=C(CH_3)COOC_2H_4O-$		$(CH_3)_3Si-O-[Si(CH_3)_2-O]_{27\,av.}-[Si(CH_2CHO-)(CH_3)-O]_{3\,av.}-Si(CH_3)_3$
XXII	ditto	ditto and 	$[[-OC_2H_4-Si(CH_3)_2-O-[Si(CH_2)_2-O]_{14\,av.}]]Si(CH_3)_2$
XXIII	$CH_2=C(CH_3)COOC_2H_4O-$		$[[-[O(CH_2)_5CO]_{5.2\,av.}-OC_2H_4-]]_2O$

TABLE I – cont'd

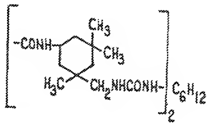
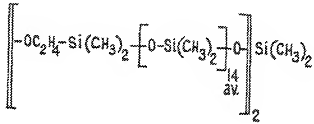
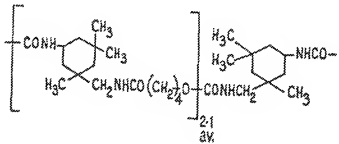
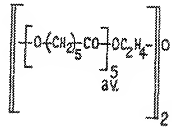
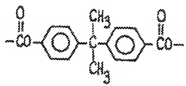
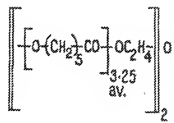
FORMULA No	"E"	"H"	"S"
XXIV	ditto		
XXV	$CH_2{=}C(CH_3)COOC_2H_4O-$		
XXVI	ditto		

TABLE 1 - cont'd

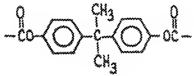
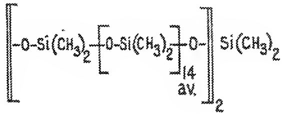
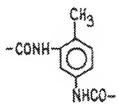
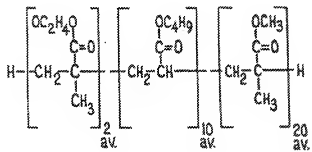
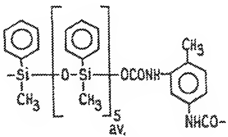
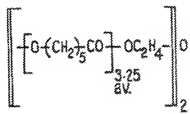
FORMULA No.	"E"	"H"	"S"
XXVII	$CH_2{=}C(CH_3)COOC_2H_4O-$		
XXVIII	ditto		
XXIX	$CH_2{=}C(CH_3)COOC_2H_4O-$		

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TABLE I - cont'd

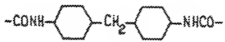
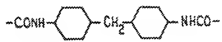
FORMULA No.	"E"	"H"	"S"
XXX	ditto		$\left[\left[O(CH_2)_5CO \right]_{1.16\ av.} OCH_2 \right]_3 CC_2H_5$
XXXI	$CH_2{=}C(CH_3)COOC_2H_4O\cdot$		$\left[\left[O(CH_2)_5CO \right]_{3.2\ av.} OC_2H_4 \right]_2 O$
XXXII	ditto	ditto	$-OC_2H_4Si(CH_3)_2O\left[Si(CH_3)_2O \right]_{29\ av.}Si(CH_3)_2-C_2H_4O-$ and $\left[-NH-CH(CH_3)CH_2-\left[OCH(CH_3)CH_2 \right]_{17\ av.}-O-C_2H_4- \right]_2 O$

TABLE I (cont'd)

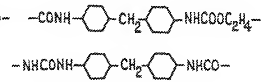
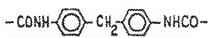
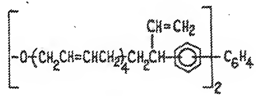
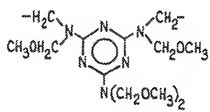
FORMULA No.	"E"	"H"	"S"
XXXIII	$CH_2{=}C(CH_3)COOC_2H_4O-$		$\left[-OC_2H_4Si(CH_3)_2\left[O-Si(CH_3)_2\right]_{14\,av.}O-\right]_2 Si(CH_3)_2$
XXIV	ditto	ditto	$\left[\left[O(CH_2)_5CO\right]_{3.25\,av.}OC_2H_4-\right]_2 O$
XXXV	$CH_2{=}CHCOOC_2H_4O-$		
XXXVI	$CH_2{=}C(CH_3)COOC_2H_4O-$		$\left[\left[O(CH_2)_5CO\right]_{3.2\,av.}OC_2H_4-\right]_2 O$

TABLE I - cont'd

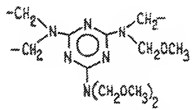
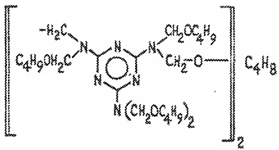
FORMULA No.	"E"	"H"	"S"
XXXVII	$CH_2{=}CHCOOC_3H_6O-$		$\left[-OC_2H_4-Si(CH_3)_2-O-\left[Si(CH_3)_2-O\right]_{14\ av.}\right]_2 Si(CH_3)_2$
XXXVIII	ditto		$\left[-\left[O-(CH_2)_4\right]_{8\cdot5\ av.}-OC_2H_4-\right]_2 O$
XXXIX	$CH_2{=}CHCOOC_3H_6O-$		$\left[-\left[O-(CH_2)_5CO\right]_{1\cdot86\ av.}-OC_2H_4-\right]_2 O$

TABLE I – cont'd

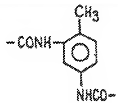
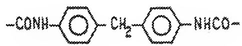
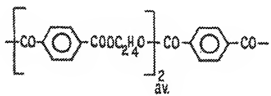
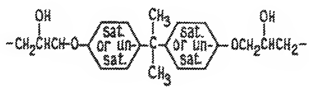
FORMULA No.	"E"	"H"	"S"
XL	ditto		$\left[\left[OC_2H_4OCOC_2H_4CO\right]_{4\ av.} OC_2H_4\right]_2 O$
XLI	$CH_2{=}CHCOOC_3H_6O-$		$\left[\left[OC_2H_4OCOC_2H_4CO\right]_{4\ av.} O\right]_2 C_2H_4$
XLII	ditto		$\left[\left[O(CH_2)_5CO\right]_{1.86\ av.} OC_2H_4\right]_2 O$
XLIII	$CH_2{=}C(CH_3)COO-$		$\left[\left[O(CH_2)_5CO\right]_{3.25\ av.} OC_2H_4\right]_2 O$

TABLE I - cont'd

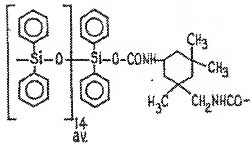
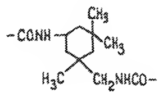
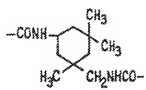
FORMULA No.	"E"	"H"	"S"
XLIV	ditto		ditto
XLV	$CH_2=C(CH_3)COO-$		$[-OC_2H_4-Si(CH_3)_2-[O-Si(CH_3)_2]_{14\,av.}-O-]_2\,Si(CH_3)_2$
XLVI	$CH_2=CHCH_2O-$		$[[O-(CH_2)_5CO]_{1.86\,av.}-OC_2H_4-]_2\,O$
XLVII	$CH_2=CHCH_2O-$		$(CH_3)_3Si-O[Si(CH_3)_2-O]_{27\,av.}[Si(CH_2CH_2O-)-O-]_{3\,av.}\,Si(CH_3)_2$

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TABLE I - cont'd

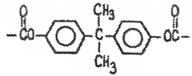
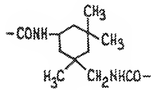
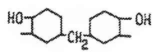
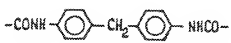
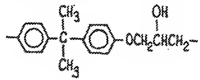
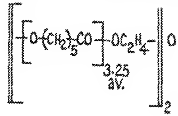
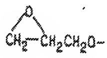
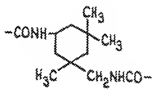
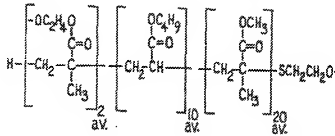
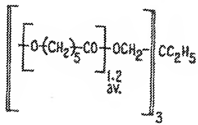
FORMULA No.	"E"	"H"	"S"
XLVIII	ditto		$\left[\left[-O-(CH_2)_5-CO-\right]_{3.25\ av.}-OC_2H_4-\right]_2 O$
XLIX	$CH_2=C(CH_3)COOC_2H_4NH-$		$\left[\left[-O-(CH_2)_5-CO-\right]_{1.16\ av.}-O-CH_2-\right]_3 CC_2H_5$
L	$CH_2=C(CH_3)CONH-$		$\left[\left[-O-(CH_2)_5-CO-\right]_{3.5\ av.}-OC_2H_5-\right]_2 O$
LI	$CH_2=C(CH_3)CH_2NH-$		$\left[\left[-O-(CH_2)_4-\right]_{8.5\ av.}-OC_2H_4-\right]_2 O$

TABLE I - cont'd

FORMULA No.	"E"	"H"	"S"
LII			
LIII			
LIV			

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Another class of oligomers useful in making the shaped articles of this invention can be represented by the general formula:

$$\left[(\text{"E"}-\text{"H"})_{\alpha}-\text{"S"}-(\text{"H"}-\text{"S"})_{\beta}\right]_{\gamma}-\text{"H"} \qquad \text{LV}$$

where "E", "H", "S", α, β and γ are as defined for formula I. Since representative species of formula LV can be made with the same "E", "H" and "S" moieties as those species of formula I listed in TABLE I (though the number and ratio of such moieties in the species of formula LV can be different than the number and ratio of such moieties in the species of TABLE I) we will omit, in the interest of brevity, a similar list of representative species of formula LV.

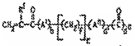
Other classes of oligomers useful in making the shaped articles of this invention can be represented by the general formulas:

$$\left[\text{"E"}(\text{"S"})_{\alpha}\left[\text{"H"}(\text{"S"})_{\alpha}\right]_{\beta}\right]_{\gamma}\text{"H"} \qquad \text{LVI}$$

and

$$\left[\left[\text{"E"}\ \text{"S"}\right]_{\alpha}\text{"H"}\left[\text{"S"}\ \text{"H"}\right]_{\beta}\right]_{\gamma}\text{"S"} \qquad \text{LVII}$$

where "H", "S", α, β and γ are as defined for formula I, but "E" in formulas LVI and VLII is represented by the formulas:



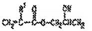
LVIII

where R^1 is hydrogen or methyl,

each A' and A'' is independently —NH— or —O—,

f is an integer of 2 to 5, and

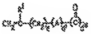
each of b, c, d' and d'' are independently zero or 1, with the provisos that (1) if b and c are both zero, then d' and d'' are both zero (in which case R^1 is preferably hydrogen), or (2) if b and c are both 1, then d' and d'' are both zero (in which case preferably R^1 is hydrogen, A' is —O—, and f is 2 or 3) or are both 1 (in which case preferably R^1 is methyl and f is 2),



LIX

where R^1 is hydrogen, or preferably, methyl,

and



LX

where R^1 is methyl or, preferably, hydrogen,

A is —NH— or, preferably, —O—,

e is an integer of 1 to 5, preferably 1, and

d' and d'' are either both zero (in which case R^1 is preferably hydrogen and e is 1) or both are 1, (in which case preferably R^1 is hydrogen, A is —NH— and e is 1).

Representative species of oligomers of formula LVI useful in making the shaped articles of this invention are set forth in TABLE II, where structural formulas for the various "E", "H" and "S" moieties of said species have been omitted in the interest of brevity, reference instead being made to structural formulas for said moieties which are set out hereinbefore. Representative species of oligomers of formula LVII can be made with the same "E", "H", and "S" moieties as those species of formula LVI listed in TABLE II (though the number and ratio of such moieties in the species of formula LVII can be different than the number and ratio of such moieties in the species of TABLE II); thus, we will omit, in the interest of brevity, a similar list of representative species of formula LVII.

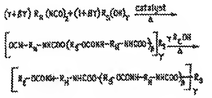
TABLE II

Formula No.	"E"	"S"	"H"
LXIII	formula LVIII where b, c, d' and d" are 1 and e is 2, R^1 is $—CH_3$, A' is —O— and A" is —NH—	XVII	XVII
LXIV	"	XXI	XXVIII
LXV		XXII	XXXVI
LXVI	formula LVIII where b, c, d' and d" are zero and R^1 is H	XXVI	XXVIII
LXVII	"	XXII	XXVIII
LXVIII	"	XXVI	XXVIII
LXIX		XL	XXXVI
LXX		XXXV	XXXVIII
LXXI		XXX	XVII
LXXII	formula LIX where R^1 is $—CH_3$,	XXII	XVII
LXXIII	"	XXVI	XXVIII
LXXIV		XIX	XXVIII
LXXV	"	XXI	XXXVI
LXXVI	formula LX where R^1 is H, A is —NH—, and d', d" and f are 1	XXVI	XXVIII
LXXVII		XL	XXX
LXXVIII	"	XXII	XXXVI
LXXIX	"	XXII	L and XVII
LXXX	formula LX where R^1 is H, d', d" and f are 1 and A is —O—	XVII	XXVI

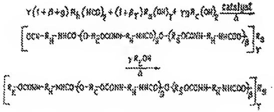
The radiation addition-polymerizable, crosslinkable oligomeric compositions useful in making the shaped articles of this invention can be prepared by general reactions that are well-known in the art of preparing addition polymerizable materials. Those general reactions are typically of two types: (1) addition reactions, viz.,the urethane- or urea-forming reaction between an active hydrogen organic compound and isocyanate or the ether-forming reaction between an active hydrogen organic compound and and epoxy compound, and (2) condensation reactions, viz., esterification or etherification of an active hydrogen organic compound with a carboxylic acid or ester or acylhalide derivative thereof or with an alkyl ether, accompanied by elimination of a byproduct; for the preparation of some oligomeric compositions, both types of reactions will be employed as shown herein after. Such reactions are commonly used in synthetic polymer chemistry, e.g. see Saunders, J. H. and K. C. Frich, "Polyurethanes: Chemistry and Technology", Part 1 (1962), especially Chapter III; Lee, H. and K. Neville, "Handbook of Epoxy Resins" (1967), especially Appendix 5—1; Bruins, P. F. "Epoxy Resin Technology" (1968), especially Chapters 1 and 2; Kirk-Othmer "Encyclopedia of Chemical Technology" 2nd Ed., Vol. 8, p.

313 (1965); Roberts, J. D. and M. C. Caserio, "Basic Principals of Organic Chemistry", p. 518 (1964). These general reactions are thus used to chemically combine "E" moieties with the "H" and "S" segments to form oligomeric compositions of use in the invention. Generally, the combining of the "E", "H" and "S" moieties is carried out in a sequence of steps; however, under some circumstances, it is convenient to carry out the reactions simultaneously and even to form the oligomeric composition in situ during the process of making the replicated plastic articles of this invention, e.g., carrying out the ether-forming addition reaction in situ in the replication mold.

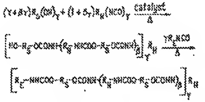
Generally, the urethane- or urea-forming reactions are carried out at temperatures from 25 to 100°C for 10 minutes to several hours or more, sufficient to bring about the reaction. Preferably, a catalyst such as dibutyltin dilaurate is used to promote the reaction. Generalized equations for such reactions in preparing the oligomeric composition used in this invention are illustrated as follows where the precursors of "H", "S" and "E" are denoted by formulas containing such letters as subscripts, the formula containing C as a subscript being a chain extending compound, and g, β and γ are as defined for formula I:



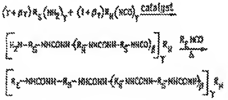
(1)



(2)

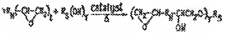


(3)

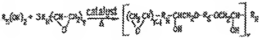


(4)

The ether-forming addition reactions are carried out generally at temperatures of 75 to 150°C (or ambient temperatures when carried out in situ in the replication of the plastic articles), preferably in the presence of catalysts such as Lewis acids, e.g., $BF_3 \cdot O(C_2H_5)_2$, or Lewis bases, e.g., benzyltrimethylammonium hydroxide, or photoactive catalysts, such as the aryl iodonium or sulfonium salts described in U.S. Pat. No. 4,081,276, when the reaction is carried out in situ. Generalized equations for such reactions in preparing the oligomer composition are illustrated as follows:

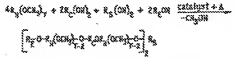


(5)

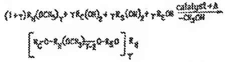


(6)

Representative ether-forming condensation reactions are those between "E" and "S" precursors having active hydrogens with an N-(lower alkoxymethyl) melamine as an "H" precursor, as illustrated by the following equations:



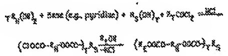
(7)



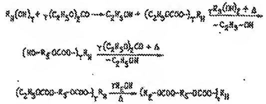
(8)

The reactions are promoted with acid catalyst such as p-toluene-sulfonic acid. Generally, temperatures from 60 to 120°C for one to three hours or more can be used. The use of reduced pressures to remove volatile lower alkanol is also desirable.

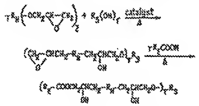
Esterification reactions are illustrated by the following equations:



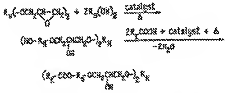
(9)



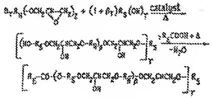
(10)



(11)



(12)



(13)

Such esterification reactions require the elimination of a byproduct (water, hydrogen halide, or lower alcohol). Esterifications are promoted by heating the mixture at 50°C to 150°C in the presence of a suitable catalyst, e.g., toluenesulfonic acid. The use of reduced pressures to remove volatile byproduct is also desirable.

Physical properties, e.g., thermal dimensional stability, of the crosslinked polymer resulting upon curing of said oligomeric composition will be dependent on the crosslink density of the polymer. An indication of that crosslink density can be derived by calculating the molecular weight per crosslink based on the monomeric precursor components of the oligomeric composition. That calculation, for example, in the case of Example 1, infra, is made by subtracting the gram moles of the "S" precursor from the gram moles of the "H" precursor, and dividing the difference into the total weight in grams of the monomeric precursor components in the oligomeric composition, the so-calculated molecular weight per crosslink being 1241. Generally, the calculated molecular weight per crosslink for the polymers will be in the range of 400 to 5000, preferably 1000 to 3000 the actual value generally being somewhat higher because of side reactions, incomplete reactions, etc.

The oligomeric products resulting from the above illustrated equations (1) to (13) have predominantly the structures shown. The oligomeric product of equations (1), (2), (5), (7), (9), and (11) are encompassed by generic formula I; those of equations (3), (4), (10), and (12) by formula LVI; those of equations (6) and (8) by formula LV; and that of equation (13) by formula LVII. For example, in the oligomeric product of equation (1), R_EO—, —CONH—R_H—NHCO—, and —O—R_S—O— correspond respectively to "E", "H", and "S" of formula I where α is 1. And in the oligomeric product of equation (2), which also falls within the scope of formula I where α is also 1, R_EO— corresponds to "E", —CONH—R_HNHCO—$($O—R_cOCONH—R_H—NHCO—$)_{\overline{b}}$ corresponds to the "H" bonded to "E", the —CONH—R_H—NHCO— moiety bonded to —OR_SO— corresponds to the "H" bonded to "S", and —OR_SO— corresponds to "S".

The oligomer products produced by these reactions often will be highly viscous and thus difficult to cast in the replication mold, and in addition may not be capable of producing the necessary crosslink density in the subsequently cured plastic article. Thus, it may be necessary to add to the oligomer product a radiation addition-polymerizable mono- or polyfunctional diluent monomer, e.g., 2-(N-butylcarbamyl) ethylmethacrylate, to lower the viscosity of the casting oligomeric composition and ensure the necessary crosslink density in the plastic article made therefrom, that crosslink density being manifested in a gel swell (determined in tetrahydrofuran, as hereinafter described) within the range of 35 to 200 wt. %, preferably 80 to 150 wt. %. Generally the amount of diluent monomer used should be less than 50 wt. % of the oligomeric composition (viz., oligomers plus diluent monomer), since greater amounts will reduce the concentration of the "H" and "S" segments below that required to provide the desired replicated plastic articles of this invention and will further increase the shrinkage during curing.

The oligomeric compositions (including the diluent monomer were used) and the articles made therefrom has the same amount of "H" segments and the same amount of "S" segments (and consequently the same ratio of these moieties). Said amount of "H" generally will be an amount in the range of 10 to 80 wt. % (of which amount at least 30 wt. % is due to the carbocyclic and heterocyclic groups), "H" preferably being 15 to 60 wt. %, and said amount of "S" will be an amount in the range of 10 to 80 wt. %, preferably 15 to 45 wt. %, the balance in the oligomeric composition being that attributable to the functional moieties "E" and the diluent monomer from which linking segments or moieties are derived as the balance of the plastic articles. Those plastic articles preferably have moduli over the temperature range of 23 to 120°C which fall on or within the boundary A—B—C—D of FIG. 1, which property is measured by the procedure described in U.S. Pat. 3,853,595 where it is referred to as "storage shear modulus, G'". The particular amounts of "H", "S" and "E" in the oligomeric composition are such that the crosslinked polymer derived therefrom preferably has such moduli. Said moduli are dependent on the "H" and "S" contents and the crosslink density of the plastic, said crosslink density being manifested in gel swell as mentioned above. If a particular oligomer composition has "H", "S" and "E" contents falling within their said ranges and yet the crosslinked polymer derived therefrom has a dynamic shear moduli curve which falls in whole or in part above the line A—B of FIG. 1, indicative of a plastic which may be too rigid for a particular article of this invention, the "H" content of the oligomeric composition will have to be lowered, e.g., by employing a higher molecular weight "S" precursor or by eliminating or decreasing the amount of chain extender in the preparation of the oligomeric composition, or the crosslink density will have to be lowered by using a higher molecular weight "H" precursor or higher molecular weight "S" precursor. On the other hand, if the dynamic shear moduli falls in whole or part below the line D—C of FIG. 1, indicative of a plastic which may be too flexible for a particular article of this invention, the "H" content of the oligomeric composition will have to be increased, e.g., by using a lower molecular weight "S" precursor and/or employing a chain extender together with additional "H" precursor, or the crosslink density will have been increased by using a lower molecular wt. "H" precursor or "S" precursor or by employing a multi-functional diluent monomer, e.g., 1,6-hexanediol diacrylate. The proper particular amounts of "H" and "S" and crosslink density for a particular system necessary to provide the preferred dynamic shear moduli defined by A—B—C—D of FIG. 1 can be readily arrived at empirically by varying the above parameters as discussed above. These adjustments of dynamic moduli are based on the generally linear relationship, on a logarithmic basis, between dynamic modulus (or tensile strength) and the amount of "H" in the cured plastic.

The materials which can be used as "H", "S" and "E" precursors in making the oligomeric compositions used in this invention, as well as chain extending agents and catalysts used in their

preparation and diluent monomers and radiation or photo sensitizers and initiators incorporated therein, are known materials, many of which are commercially available. An illustrative description of those materials follows below, reference being made to patents and the literature for purposes of brevity.

Polyols which can be used as said "S" precursors include polyester polyols, such as the lactone polyesters described in U.S. Pat. No. 3,169,945 (especially the polyesters terminated with 2 or more hydroxyl groups formed by reaction of epsilon-caprolactone and a polyol, polyamine or amine alcohol), the hydroxyl-terminated polyester condensation polymers described in U.S. Pat. No. 3,641,199, the substantially linear, saturated, hydroxy-terminated polyesters described in U.S. Pat. No. 3,457,326 the hydroxy-containing polyesters described in U.S. Pat. No. 3,931,117, and the hydroxy-terminated block polymers of polyethers and polyesters described in U.S. Pat. No. 3,960,572. Polyether polyols useful as said "S" precursors include the hydroxy-terminated polyether condensation polymers described in U.S. Pat. No. 3,641,199, the substantially linear, saturated hydroxy-terminated polyethers described in U.S. Pat. No. 3,457,326, the polyalkylene ether polyols described in U.S. Pat. No. 3,499,852, 3,697,485, and 3,711,444, and the polyethylene glycols and polypropylene glycols described in U.S. Pat. No. 3,860,770. Polyolefin polyols useful as "S" precursors include those described in U.S. Pat. No. 3,678,014 and the α,ω-diols from ethylene described in J. Polymer Science, Part A—1, Vol. 5, p. 2693 (1967). Polysiloxane polyols useful as "S" precursors include the hydroxy-terminated diorganopolysiloxanes in U.S. Pats. 4,098,742 and 3,886,865, and the siloxanes having a reactive hydroxyl group bonded to at least 2 of its silicon atoms, described in U.S. Pat. Nos. 3577,264, 3,976,676, and 4,013,698.

A particularly useful, commercially available class of caprolactone polyols which can be used as "S" precursors are those sold under the Trademark "NIAX", such as PCP—0200, PCP—0210, PCP—0230 and PCP—0300 (e.g., see technical bulletin F—42464 of Union Carbide Corp.). Other useful commercially available "S" precursors are the polyoxypropylamines sold under the trademark "Jeffamine", such as D—2000, and silicone polycarbinols sold under the trademark "DOW CORNING", such as Q4—3667.

Polyisocyanates, especially diisocyanates, which can be used as "H" precursors, include those described in U.S. Pat. Nos. 3,641,199; 3,700,643; 3,819,586; 3,878,036; 3,931,117; 3,960,572; and 4,065,587. Epoxides which can be used as "H" precursors include diglycidyl ethers of bisphenol A, diglycidyl isophthalate, diglycidyl phthalate, o-glycidyl phenyl glycidyl ether, diglycidyl ethers of resorcinol, triglycidyl ethers of phloroglycinol, triglycidyl ethers of methyl phloroglycinol, diglycidyl phenyl ether and diglycidyl ether of hydrogenated bisphenol A, all of which are described in Appendix 4—1 of "Handbook of Epoxy Resins", by H. Lee and K. Neville, McGraw-Hill Book Company (1967).

Particularly useful commercially available diisocyanates which can be used as "H" precursors include isophorone diisocyanate sold under the trademark "IPDI" by Veba-Chemie AG and methylene bis(4-cyclohexylisocyanate) sold under the trademark "Hylene" WS by DuPont.

"E" precursors which can be used include the acrylyl compounds described in U.S. Pat. No. 3,700,643, the hydroxy acrylates and methacrylates described in U.S. Pat. No. 3,577,262 the ethylenically-unsaturated alcohols described in U.S. Pat. No. 3,297,745, the hydroxyalkyl-acrylates and methacrylates described in U.S. Pat. No. 4,065,587, the ethylenically unsaturated alcohols described in U.S. Pat. No. 3,960,572 and the following epoxides: butyl glycidyl ether, diglycidyl ether of propylene glycol, diglycidyl ether of butanediol, vinylcyclohexene dioxide, mixed isomers of bis (2,3-epoxycyclopentyl)ether, bis(3,4-epoxy-6-methycyclohexylmethyl) adipate, bis(3,4-epoxycyclopentyl)ether, 3,4-epoxy-6-methylcyclohexane carboxylate, para-butylphenol glycidyl ether, limonene dioxide, dicyclopentadiene dioxide and 3,4 epoxy-t-methylcyclohexylmethyl-4-epoxy-6-methylcyclohexane carboxylate, all of which epoxides are described by Lee and Nevill, supra.

Chain extenders which can be used in preparing the oligomers used in this invention include the known hydroxy-, carboxy-, amino or mercapto-terminated compounds useful for that purpose (see U.S. Pat. No. 3,448,171)

To promote oligomer-forming reactions, it is generally desirable to utilize a catalyst. Typical examples of such catalysts include compounds containing tertiary amino groups, tin compounds and titanium compounds.

Examples of the preferred tin compounds are dibutyltin dilaurate, dibutyltin diethylhexoate, dibutyltin sulfide, dibutyltin dibutoxide, stannous octoate, stannous oleate and stannous chloride. Concentrations of catalyst from about 0.01 to about 0.5 percent and preferably about 0.025 to 0.1 percent by weight of the total weight of reactants (exclusive of solvents) can be used.

The diluting monomers are addition-polymerizable monomers, viz., ethylenically unsaturated monomers and vicepoxy reactive diluents. The diluting monomers contribute to the "H", "S" or "E" content of the oligomeric composition depending on the glass transition temperature, T_g, of a homopolymer of the particular monomer. If the T_g of its homopolymer is above about 350°K, the monomer contributes to the "H" content, below about 250°K to the "S" content, and between about 250°K and 350°C to the "E" content. The concept of "hard" and "soft" monomers is well known (e.g., U.S. Pat. Nos. 4,077,926 and 4,077,932) and has been used to describe monomers to be optionally used in adhesive compositions.

Suitable ethylenically unsaturated diluting monomers and the glass transition temperature of their homopolymers are well known in polymer chemistry literature, e.g., Brandrup and Immergut, Polymer Handbook, III—61 to 73, Interscience Publishers (1967). Examples of the "hard" monomers (and the T_g of their homopolymers) are isobornyl acrylate (367°K), methyl methacrylate (378°K), cyclohexyl chloroacrylate (372°K), 2-chlorostyrene (392°K), 2,4-dichlorostyrene (406°K), styrene (373°K), acrylic acid (360°K) acrylamide, acrylonitile (393°K) and methacrylonitrile (393°K). Examples of the "soft" monomers (and the T_g of their homopolymers) are butyl acrylate (218°K), ethyl acrylate (249°K), 2-ethylhexyl acrylate (223°K), dodecyl methacrylate (208°K), and 4-decylstyrene (208°K). Examples of diluting monomers which contribute to neither the "hard" content or to the "soft" content but become incorporated into the linking segments (and the T_g of their homopolymers) are 4,cyclohexyl-l-butene (318°K), 1-dodecene (267°K), t-butyl acrylate (251°K), cyclohexyl acrylate dodecyl acrylate (270°K), isopropyl acrylate (270°K), methyl acrylate (279°K), butyl methacrylate (293°K), 4-butoxystyrene (320°K), 2-(N-butylcarbamyl)ethyl methacrylate (304°K) and 2-(N-ethylcarbamyl)ethyl methacrylate. Polyethylenically unsaturated monomers also become incorporated into the linking segments and are used in small quantities to reduce the molecular weight of the cured oligomeric composition per crosslink. Typical of such compounds are 1,4-butylene dimethacrylate or acrylate, ethylene dimethacrylate or acrylate, trimethylolpropane di- or tri-acrylate, glyceryl diacrylate or methacrylate, glyceryl triacrylate or methacrylate, glycidyl acrylate or methacrylate, pentaerythritol triacrylate or trimethacrylate, diallyl phthalate, 2,2-bis(4-methacryloxyphenyl)-propane, diallyl adipate di(2-acryloxyethyl)ether, dipentaerythritol pentaacrylate, neopentylglycol triacrylate, polypropylene glycol diacrylate or dimethacrylate, and 1,3,5-tri-(2-methacryloxyethyl)-*s*-triazine.

Diluting epoxy-reactive monomers include phenyl glycidyl ether, 4-vinylcyclohexene dioxide, limonene dioxide, 4-vinyl-cyclohexene oxide, 1,2-cyclohexene oxide, glycidyl acrylate, glycidyl methacrylate, and styrene oxide.

Suitable addition-polymerization catalysts for use in the oligomeric compositions wherein the addition-polymerizable group is an ethylenically unsaturated group as represented in formula II, viz., acrylic or olefinic, are catalysts which liberate or generate a free-radical on addition of energy. Such catalysts are well known and are described frequently in polymerization art, e.g., Chapter II of "Photochemistry" by Calvert and Pitts, John Wiley & Sons (1966). Included among free-radical catalysts are the conventional heat activated catalysts such as organic peroxides and organic hydroperoxides; examples are benzoyl peroxide, tertiary-butyl perbenzoate, cumene hydroperoxide, azobis (isobutyronitrile) and the like. The preferred catalysts are photopolymerization initiators which, when used in an addition-polymerizable group-containing composition, facilitate polymerization when the composition is irradiated. Included among such initiators are acyloin and derivatives thereof, such as benzoin, benzoin methyl ether, benzoin ethyl ether, benzoin isopropyl ether, benzoin isobutyl ether, and α-methylbenzoin; diketones such as benzil and diacetyl, etc.; organic sulfides such as diphenyl monosulfide, diphenyl disulfide, decyl phenyl sulfide, and tetramethylthiuram monosulfide; S-acyl dithiocarbamates, such as S-benzoyl-N,N-dimethyldithiocarbamate; phenones such as acetophenone, α,α,α-tribromacetophenone, α,α-diethoxyacetophenone, o-nitro-$\alpha,\alpha\alpha$-tribromoacetophenone, benzophenone, and p,p'-tetramethyldiaminobenzophenone; sulfonyl halides such as p-toluenesulfonyl chloride, 1-naphthalene-sulfonyl chloride, 2-naphthalenesulfonyl chloride, 1,3-benzenedisulfonyl chloride, 2,4-dinitrobenzenesulfonyl bromide and p-acetamidobenzenesulfonyl chloride. Normally, the initiator is used in amounts ranging from about 0.01 to 5% by weight of the total oligomeric composition. When the quantity is less than 0.01% by weight, the photo polymerization rate becomes extremely low. If the initiator is used in excess of 5% by weight, no correspondingly improved effect can be expected. Thus, addition of such greater quantity is economically unjustified. Preferably, about 0.25 to 1.0% of initiator is used in the oligomeric compositions.

For those oligomeric compositions in which the radiation sensitive addition-polymerizable, functional group-containing moiety is an epoxy group as represented in formulas III, IV, any catalyst can be used which liberates or generates a cationic polymerization catalyst upon exposure to radiation. These catalysts are onium salts that are well known in the art of polymerization, e.g., U.S. Pat. No. 3,826,650 in which it is taught that photosensitive latent curing agents classified as aromatic diazonium salts of a complex anion, e.g., hexafluoroantimonate, and the like are used for photopolymerizing epoxy monomers, and U.S. Pat. No. 4,081,276 in which it is taught that photoinitiators capable of releasing a cationic polymerization catalyst upon exposure to radiant energy are aromatic halonium, aromatic Group Va onium, and aromatic Group VIa onium salts of complex anions and are suitable for forming an image on a substrate. The preferred catalyst for polymerizing the oligomeric compositions of the invention in which addition-polymerizable functional group-containing moiety is an epoxy group are aromatic iodonium or sulfonium salts of complex anions selected from tetrafluoro borate, hexafluorophosphate, hexachloroantimonate, hexafluoroantimonate. Examples of such salts include diphenyliodonium hexafluorophosphate, diphenyliodonium hexafluoroantimonate, triphenylsulfonium hexafluorophosphate, and triphenyl hexafluoroantimonate. Other preferred aromatic onium salt photoinitiators are the aromatic iodonium and sulfonium salts of fluoroaliphatic sulfonic acid and the bis(fluoroaliphaticsulfonyl)methanes that are disclosed in U.S. Pat. No. 4,049,861.

In making a particular shaped plastic article of this invention for a specific application, economic

considerations will influence what particular oligomeric composition or compositions and the mode of preparation thereof should be used for that purpose. For example, in making retroreflective cube corner sheeting for use as highway traffic control markers where such requirements as resistance to weathering and high impact strength are essential, urethane-containing oligomeric compositions preferably would be selected, such as those within the scope of formulas I or LV, the urethane linkage imparting stability to the sheeting upon its exposure to light, heat and moisture, and the mode selected for making such oligomeric composition advantageously being that of aforesaid equation (2) because, for example, it involves only two reactions steps and results in an oligomeric product with a relatively high content of "H" segments, necessary for satisfying the high impact strength requirement of the sheeting, and because equation (2) permits the use of hydroxyacrylates, such as 2-hydroxyethylmethacrylate, cycloliphatic polyisocyanates, such as isophorone diisocyanate, and polyester polyols, such as polycaprolactone diols, these three types of reactants being commercially available raw materials which will augment that of the urethane linkage in providing the desired degree of weatherability.

As another example, in making flexible video discs, where high abrasion resistance and optical transparency are important, urethane-containing oligomeric composition preferably would be selected, such as those falling within the scope of formulas I or LV, the urethane linkage imparting abrasion resistance to the disc, and the mode selected for making such oligomeric composition advantageously being that of aforesaid equation (1) because, for example, of its limited number of reactions and its amenability to use of reactants whcih are commercially available and which impart to the disc requisite flexibility, high optical transparency, and low haze; such reactants are cycloaliphatic polyisocyanates, such as isophorone diisocyanate, polyester or polyether polyols, such as polycaprolactone or polytetramethylene glycol, and hydroxyacrylates, which also are commercially available and which also impart to the oligomeric composition the property of fast radiation curability.

As still another example, in making Fresnel lenses where high optical transparency is important for image projection and high focusing efficiency is important for solar heat concentration, urethane-containing or aromatic carbonate-containing oligomeric compositions preferably would be selected, such as those within the scope of formulas I or LV, the urethane linkage imparting stability to light and heat and the aromatic carbonate moiety imparting high refractive index and concomittant low chromatic aberration, and the mode selected for making said urethane-containing oligomeric compositions advantageously being that of equations (1) and (2) and the mode for making said carbonate-containing oligomeric compositions advantageously being the aforesaid equations (9) or (10), said equations (1), (2), (9) and (10) entailing a limited number of reactions and being amenable to use of commercially available materials as reactants for imparting the requisite properties to the plastic articles. In the case of projection lenses and solar collectors, said reactants can be isophorone diisocyanate, polycaprolactone polyols, and hydroxyacrylates.

The shaped plastic articles of this invention are typically prepared by pouring or filling a mold master with the oligomeric composition, exposing the resulting cast composition to actinic radiation to rapidly cure the same, and removing from said mold master the resulting shaped plastic article which comprises crosslinked plastic and has a surface bearing microstructure replicated from the mold master.

The particular mold master used in replication will depend on the type of shaped article to be made. For purposes of making optical lenses, e.g. ophthalmic lens blanks, having a surface with an optical finish, the mold master can be made of transparent (e.g., "Pyrex") glass, such masters being commercially available. For purposes of making diffraction gratings, e.g., spectral filters, light collectors, and decorating decals, the mold master can be made of metal with the diffraction pattern thereon made by mechanical ruling or holographically, such diffraction grating masters being commercially available, e.g., see the "Diffraction Grating Catalog" (1974), of PTR Optics Corp., Waltham, Mass., and Bulletins ACA 1004-1-1270 and ACA 1006-1-1-270 of Angenieux Corp. of America, Oceanside, N.Y.

For cube-corner sheeting, linear Fresnel lenses, and other shaped plastic articles having raised or indented microstructure-bearing surfaces, mold masters can be used which are made of plastic, e.g., acrylonitrile-butadiene-styrene, or preferably (for mass production of such replicated articles) made of metal fabricated directly from a suitable metal by engraving, hobbing, assembling as a bundle a plurality of metal parts machined in the desired configuration, or other mechanical means or by electroforming, e.g., see "Encyclopedia of Polymer Science & Technology", VOl. 8, p. 651 (1968), and "Principles of Electroplating and Electroforming", W. Blum and G. B. Hogaboom, 3rd Ed. McGraw-Hill Co., Inc., Chap. VIII (1949), and U.S. Pat. No. 3,689,346.

Where the microstructure to be replicated can be initially formed by machining originals made of plastics which are difficult to wet, such as commercially available acrylic resins, e.g. that sold under the trademark "LUCITE", electroformed metal mold masters can be formed from such machined originals and used to make shaped plastic articles (such as the diffraction gratings, Fresnel lenses and retroreflective sheeting described in the working examples of this specification) by treating the machined plastic surface to render it wettable and sensitized (for example, by the treatment described in U.S. Pat. No. 3,666,527), rendering the surface conductive by simultaneous contact, using a two-nozzle spray gun, with an ammonical silver salt solution, and a reducing agent, such as formaldehyde or dextrose, plating or electroforming nickel on the silver-coated surface from a commercially available

nickel bath, and separating the resulting metal layer from the plastic original, thus generating a metal master which can be used for replicating said shaped plastic articles or from which second and third generation electroformed nickel copies can be made as required to provide a tooling supply for replicating said shaped plastic articles. Where the microstructure to be replicated cannot be initially machined on a plastic original for purposes of making masters used in replicating such articles as the video disc described hereinafter in a working example of this specification, mold masters fabricated by photoresist techniques can be used, e.g., see the journal articles in "Science", Vol. 196, No. 4293, p. 945 (1977), and "Optics and Laser Technology" August, 1977, p. 169.

The cast, curable oligomeric composition can be cured by exposure to actinic radiation, viz., ionizing or non-ionizing radiation, a curing technique well-known and widely-used in the art of radiation addition polymerization (e.g., see U.S. Pat. No. 3,700,643). Typically, ultraviolet radiation produced by such sources as mercury arcs, sunlamps, or xenon lamps, with UV radiation primarily in the regions of about 2000 to 4000A, will be most useful. Ionizing radiation produced by electron accelerators, e.g., continuous filament or swept beam accelerators, can be used, wherein the electrons are provided with the kinetic energy derived from acceleration through a field varying from 150 kilovolts up to as high as 4000 kilovolts. Useful radiation dosage required to complete the curing will vary, depending on the particular oligomeric composition used, its molecular weight and the crosslinking density desired; for ultraviolet radiation, a useful dosage will generally be in the range of 0.1 to 100 joules per square centimeter exposed and for ionizing radiation, such as electron beam, a useful dosage will be 5×10^{3} rads to 10^{7} rads. Normally the exposure is carried out at or near room temperature and atmospheric pressure. An inert atmosphere, such as nitrogen or carbon dioxide gases, may be desired in curing some oligomeric compositions, viz., those relying on free-radical curing mechanisms, e.g., acrylate-, or methacrylate-terminated oligomers. Radiation processing equipment useful in the practice of this invention is commercially available, e.g., untraviolet lamp systems sold by Radiation Polymer Corp., Plainfield, Illinois, and Fusion Systems Corp., Greenbelt, Maryland, and ionizing radiation systems sold by Energy Sciences, Inc., Burlington, Mass. and Radiation Dynamics, Inc., Long Island, N.Y. (Although the radiation used in curing the oligomeric composition has been described in detail herein as being actinic radiation, thermal radiation can be used, e.g., 50° to 150°C for 5 min. to several hours depending on the oligomeric composition and catalyst used; thermal radiation is not preferred because it is more time-consuming, requires more energy, and is not as controllable as actinic radiation).

Following radiation of the cast composition (actinic radiation effects complete curing in 1/2 to 5 seconds generally), the cured, shaped plastic article is readily separated or removed from the mold master. Mold release agents may be used, though generally they are not required. Depending on the particular shaped plastic article made and the nature of the mold master, the mold master can be repeatedly used for replication done on a continuous mass production basis.

In selecting an oligomeric composition for use in preparing a particular shaped article, it has been found useful to prepare a transmissive diffraction grating test sample from the composition. Such sample can be used to measure replicating fidelity capability of the oligomeric composition and the thermal dimensional stability capability of the oligomeric composition. FIG. 2 schematically illustrates a replicated diffraction grating useful as a test sample, the preparation and testing of which is described hereinafter. The test measures the first order diffraction efficiency of both the master grating and replicated test sample, the efficiency of which is related to the depth of the grooves. A comparison of the efficiency of the replicated test sample to that of the master grating determines the fidelity of replications. Generally the oligomeric composition of this invention will give diffraction grating test samples having a replicated efficiency of at least 85% of that of the master grating. For some particular shaped articles, the replication efficiency must be significantly greater than 85% (for example, for replicated video discs, the replication efficiency must approach at least 99%) and for such articles an oligomeric composition must be selected which will produce a diffraction grating test sample having such replication efficiency. Replication efficiency will be dependent on the degree of shrinkage of the diffraction grating test sample; the greater the shrinkage, the lower the replication fidelity. Shrinkage in turn is dependent on the number of double bonds present in the oligomeric composition per unit weight thereof, and generally the greater such number of double bonds, the greater the degree of shrinkage. For acrylate- or methacrylate-terminated oligomers, the shrinkage will be about 20 cc/gram mole of double bonds, and this shrinkage factor can be used as a guide in selecting an oligomeric composition necessary to yield the desired replication efficiency.

Generally, the oligomeric compositions will yield diffraction grating test samples which have high thermal dimensional stability. For example, generally when said test samples are heated in air in a programmed manner from 23° to 170°C, the first order diffraction efficiency is practically constant over these temperatures. (By contrast, the first order diffraction efficiency of comparative diffraction grating test samples made of poly(methyl methacrylate), polyvinyl chloride, cellulose acetate butyrate, and polyethylene terephthalate dropped rapidly or precipitously to zero when the temperature reached about 70 to 115°C). The change in first order diffraction efficiency of diffraction grating test samples of the oligomeric compositions of this invention upon heating at 130°C in air for 1 hour is less than 15%, as compared to the first order diffraction efficiency before heating. Generally, the higher the weight ratio of "H" to "S" in the oligomeric composition, and the lower the molecular weight between crosslinks in

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the shaped article produced therefrom, the greater the thermal dimensional stability, i.e., the smaller the change in first order diffraction efficiency upon heating.

Some of the shaped articles of this invention will require higher thermal dimensional stability than others, viz., a change in first order diffraction efficiency on heating at 130° of less than 5%. For example, replicated cube-corner sheeting, the use of which exposes it to elevated temperatures, e.g., on a road sign heated by the sun in Arizona, will require a high thermal dimensional stability, whereas a replicated video disc, played at room temperature, will not require high thermal dimensional stability.

In addition to the preparation of diffraction grating test samples, it has been found useful to prepare cured, self-supporting film samples (with planar surfaces) of the oligomeric composition and measure the tensile strength, elastic modulus, elongation-to-break, and dynamic shear moduli of the film samples, the preparation and testing of which is described elsewhere herein. The values of these measurements will be factors to consider in selecting an oligomer composition for fabrication of a particular shaped plastic article therefrom. For example, a replicated video disc which may have to be relatively limp (or "floppy") for playing on a particular type of player, would be prepared from oligomeric compositions which yield test film samples having relatively low elastic modulus and dynamic shear moduli and relatively high elongation. In contrast, a rigid or still replicated Fresnel lens, used for projection of images, would be prepared from oligomeric compositions which yield test film samples having relatively high elastic modulus and dynamic shear moduli, and relatively low elongation. The test film samples can also be measured for optical properties as an aid in selection of an oligomeric composition for preparation of replicated shaped plastic articles used for optical purposes, e.g., where it is necessary to satisfy requirements of high transmission (i.e., at least 90%) and low haze (i.e., less than 5%, preferably less than 2%).

FIGS. 3 and 4 schematically illustrate a portion of a typical replicated cube-corner retroreflective sheet 1 made in accordance with this invention. The geometry or configuration of this type of article is described, for example, in U.S. Pat. No. 3,810,804. Reference 2 generally designates one of the minute cube corner elements or formations disposed in an array on one side of the sheeting 1. Each element 2 has the shape of a trihedral prism with three exposed planar faces, substantially perpendicular to one another, with the apex of the prism vertically aligned with the center of the base. The angle between the faces is the same for each cube-corner element in the array, and will be about 90°. Said angle can slightly deviate from 90° by design, i.e., the angle will be dependent upon the particular application of the sheeting, as is well-known. For example, in the United States, state governments generally specify maximum brightness of retroreflective traffic control markers at from 0.2° to 2° divergence (or observational) angles, thus dictating a specific angle between the faces of the cube-corner elements in the marker. The cube corner elements 2 in sheet 1 are all of the same dimensions and are aligned in an array or pattern of rows and columns, the bases being in the same plane, and adjacent elements being contiguous at the edges of their bases such that there is no spacing or flat areas between adjacent elements. The cube-corner elements 2 surmount a body portion 3, the lower surface of which is smooth or planar, the body portion being preferably integral with elements, the sheeting thus being monolithic. Generally, each cube-corner element 2 has a side edge dimension up to 0.025 inch (0.635 mm), preferably less than 0.010 inch (0.254 mm). The body portion 3 is sufficiently thick to render the sheeting self-supporting and tough so as to maintain the integrity of the array of cube-corner elements 2. Generally, the body portion will be 0.002 to 0.030 inch (.05 to .075 mm), preferably 0.003 to 0.010 inch (0.075 to 0.25 mm).

In the application of such cube-corner sheeting as a highway traffic control marker, it will be desirable to seal air spaces between the faces of the cube-corner elements with a sealing film placed over the top of the elements e.g., in the manner described in U.S. Pat. No. 4,025,159, and coat the exposed surface of the film with a pressure-sensitive adhesive composition which is dried and adhered to a rigid sheet, e.g., aluminum, which forms a base for the resulting marker. The exposed lower surface 8 of the body portion 3 of the cube-corner sheeting 1 may be first selectively coated with transparent ink layers to provide the desired traffic control message, e.g., "STOP", and then coated with a top coat to protect the message, e.g., against weathering.

The principle of operation of retroreflective cube corner structures is well known, e.g., see J. Optical Society of America, Vol. 48, No. 7, July, 1958, p. 498. That principle is in essence illustrated by FIG. 5. Referring to that figure, in which a single cube corner element 2 is shown schematically with two of its faces 6, 7 being substantially perpendicular to one another, as shown by the angle $90°\pm\theta$, and the body portion 3 having an exposed lower surface 8. An incident ray of light I enters the element 2 upon striking surface 8 in a direction perpendicular thereto, passes through the body portion 3, strikes face 6, is reflected to the other faces, is reflected from the latter and passes out of the element as reflected ray I'. Perfect retroreflection of incident ray I for the particular element shown in FIG. 5 would result in the reflected ray passing out the element in a path, shown by the broken line, exactly parallel to the path of the incident ray. The deviation between the path of perfect reflection and the actual path, I', is shown by the divergence angle δ, which will be 0.2° to 2° in the case where state governments specify the same as described above. In order to obtain and maintain the desired specified divergence angles, the desired dimensions and angles of the cube-corner elements must be obtained and maintained within very narrow limits. For example, as described by J. Optical Society of America, supra, for a plastic having an

index of refraction of 1.5 (typical for the plastics comprising the shaped articles of this invention, said plastics generally having an index of 1.48 to 1.6), the divergence angle δ can be expressed by the equation δ=4.9 θ, and thus when δ is 0.2°, θ is 0.041° or 8.8 minutes of arc, which is an exceedingly small angle. If the angles between the faces of a replicated cube-corner element cannot be controlled and maintained, e.g., because of shrinkage, distortion upon removal from the mold, or of thermal distortion, the efficiency of retroreflection will be affected. Even a slight lack of control and maintenance of the angle can significantly adversely affect the efficiency. Rigid, high elastic modulus plastics, such as poly (methyl methacrylate), have thus been resorted to in the art, however, such plastics are brittle and have low heat distortion resistance. In contrast, the desired angles of the plastic cube corner elements made in accordance with this invention are controlled and maintained even at elevated temperatures, and the elements are flexible, articles with such elements being of wide application, e.g., where high impact strength is desired or required, as in the case of highway "STOP" sign. Additionally, the retroreflective cube-corner sheeting of this invention can be made with initial high brightness capability, e.g., at least 600 candles/lumen at 0.2° divergence angle.

FIG. 4A illustrates the combination of the replicated cube-corner retroreflective sheet 1 of FIGS. 3,4 with a retroreflective beaded sheet 14, this type of construction being described in U.S. Pat. No. 4,025,159, as a combination cube-corner exposed-lens product of the general type described in U.S. Pat. No. 3,140,340. Sheet 14 comprises a layer 15 of binder material, a monolayer of transparent glass microspheres 16 partially embedded in the binder material, and specular reflective material 17 underlying and in optical connection with the embedded surface of the microspheres. The points of contact between the apices of cube-corner elements 2 and microspheres 16 can be bonded as shown in FIG. 4A and as taught in U.S. Pat. No. 4,025,159, forming hermetically sealed cells or pockets 18, or the sheets 1 and 14 can be spaced apart as taught in U.S. Pat. No. 3,140,340, forming an air gap which provides a prism-air interface. In this construction, light rays escaping from the cube-corner sheet 1 are reflected back from beaded sheet 14, thereby providing wide angularity and divergence of retroreflection.

Other articles of this invention are echelon or Fresnel lenses, such as those with configurations described in U.S. Pat. Nos. 3,334,958, 3,972,593, 3,511,563, and 4,082,433, and used, for example, in overhead projectors. FIG. 6 illustrates a plurality of one type of such lens 9, viz., linear Fresnel lenses (fabricated in accordance with this invention, as shown herebelow) in the form of a continuous sheet 10 of contiguous replicated plastic lenses, which sheet can be cut to separate the individual lenses. The flexibility and dimensional stability of the Fresnel lens made in accordance with this invention makes them useful in a wide field of application, such as decorative mouldings, e.g., automobile moulding, described in U.S. Pat. No. 3,908,056.

As mentioned hereinbefore, replicated shaped plastic articles can be fabricated in accordance with this invention for purposes of information processing and transmission. FIGS. 7 and 8 illustrate an example of such articles, namely a video disc 11 (the fabrication of which is exemplified hereinafter) having spirally arranged tracks 12 each of which is made up of circumferentially-spaced, minute depressions or holes commonly called "micropits", with lengths, for example, about 1.2 μm, widths about 0.75 μm, and depths about 0.3 μm, and which are circumferentially spaced, for example 1.5 μm, the variations of said lengths and spacings depending on the frequency of the carrier signals which are recorded on the disc, articles of this type being described in Optics & Laser Technology, supra. (Alternatively, the information on the video disc can be in spiral grooves with the video information appearing on the bottom and wall regions of the grooves in the form of geometric or topographical variations, as described, for example, in U.S. Pat. Nos. 3,795,534 and 3,882,214.). The high replication fidelity capability of this invention is particularly well-suited to fabrication of the above-described replicated video discs.

Objects and advantages of this invention are illustrated in the following examples thereof. In these examples, the parts referred to are parts by weight and the percents referred to are percents by weight. In all runs in which the addition polymerizable oligomer products were synthesized, a dry air atmosphere was maintained during the course of reaction. The cured film test samples used for measuring physical properties were made by mixing 100 parts of the oligomer product (or oligomer product diluted with diluent monomer) with 0.5 part 2,2-diethoxyacetophenone photoinitiator, vacuum degassing the resulting mixture to remove entrapped air, and casting the mixture to a thickness of 250 microns (using a flat-bed knife coater) between two sheets of 125-micron thick polyethylene terephthalate polyester, thereby forming a "sandwich" assembly. Using a laboratory ultraviolet processor (viz., a "QC Processor", manufactured by Radiation Polymer Corp.) the "sandwich" assembly was passed six times on a moving belt conveyor moving at 15 m per minute under a bank of two medium pressure mercury vapor arc lamps operating at 80 watts/cm of length. The conveyor was spaced at a distance of 10 cm from the lamps. At the completion of the curing process, the cast mixture cured to a solid film of crosslinked polymer between the polyester sheets, which were then stripped from the polymer film and physical properties of the film were then tested.

The replicated diffraction grating test samples (used for measuring replicated fidelity and thermal dimensional stability) were made in the following examples by using a high frequency holographic metal mold diffraction grating master, having 867.7 line pairs per millimeter. This master was coated (by a

flat-bed knife coater) with a 375-micron thick layer of the oligomer product (or oligomer product diluted with diluent monomer), to which 0.5 percent 2,2-diethoxyacetophenone had been added. A polyethylene terephthalate polyester film (125-micron thick) was placed as a cover sheet over the layer of curable oligomer material and the resulting construction was cured with said "QC Processor" by placing it on a conveyor moving at 15 metres per minute under two medium pressure mercury vapor lamps operating at 80 watts per cm of length. A distance between the lamps and the oligomer surface of 10 cm was maintained. After six passes under the lamps, polymerization of the oligomer product was complete. The polyester cover sheet was stripped off and the layer of polymerized product (a replicated diffraction grating) was separated from the master and used as a test sample. The first order diffraction efficiency of the test sample was measured by the procedure described by Beesley et al in J. Applied Optics, Vol. 9, No. 12, Dec. 1970, p. 2720, and the diffraction efficiency of the test sample was calculated. The test sample was then placed in a forced air circulating oven at 130°C for one hour. After this heat treatment, the first order diffraction efficiency was again measured and the percent difference from the original value was taken as the measure of the resistance of the test sample to thermal distortion.

The diffracting grating test samples were also used to determine the gel swell of the crosslinked polymers as an indication of the degree of crosslinking thereof (although the gel swell of the cured film samples could also have been used for this purpose). The gell swell was determined by immersing a sample portion of known weight, W_1 (about 0.5 g), of the diffraction grating test sample in 25 ml tetrahydrofuran solvent (analytical reagent grade) for 24 hours at about 23°C, removing the resulting swelled sample portion, wiping or padded off the adhering film of solvent from the sample portion and quickly determining its weight, W_2. The used solvent was evaporated to dryness and the weight, W_3, of the dried residue (the solubilized fraction of the sample portion) was determined. The weight percent gel swell of the tested crosslinked polymer was calculated by the formula:

$$\%\ \text{gel swell} = \frac{W_2 - W_3}{W_1} \times 100$$

The lower the percent gel swell, the greater the degree of crosslinking (see "Encyclopedia of Polymer Technology", Vol. 4, p. 63—65, published by Interscience Pub. (1966)).

EXAMPLES 1—6

Into a 4-liter metal reactor, immersed in an oil bath and equipped with a propeller agitator, thermometer, addition funnel, and dry air sparger extending into the reactor through the lid thereof, there were charged 667 g (3 moles) isophorone diisocyanate ("IPDI") and 0.05 g stannous chloride. When the diisocyanate reached 70°C, there was then added from the addition funnel 795 g (1.5 moles) warm polycaprolactone diol ("NIAX" PCP 0200) while agitating the reactor contents and maintaining the same at about 70°C. The resulting mixture was agitated for 13 hours at 70°C to prepare the isocyanate-terminated, polycaprolactone urethane prepolymer after which 400 g (3.05 moles) 2-hydroxyethyl methacrylate was added over a 3.5-hour period. The resulting condensation reaction was allowed to proceed for 13 hours at 70°C until inspection of withdrawn samples by infrared analysis revealed that essentially no residual isocyanate was present in the reaction mixture. Infrared analysis verified that the resulting oligomer product comprised acrylate-capped polycaprolactone urethane oligomer having essentially the structure shown by formula XVII. This oligomer product had a calculated composition of 35.8% "H" segments, 43.0% "S" segments, and 21.2% addition polymerizable groups.

Cured film and replicated diffraction grating test samples were prepared from the oligomer product and the properties of these articles were measured and the amounts of the various segments and crosslink density of the cured oligomer product were calculated. The results were tabulated in TABLE III together with the results obtained for film and diffraction grating test samples prepared from the oligomer product diluted with various amounts of diluent monomer.

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TABLE III

Ex.	Amount of diluent[a] used %	Cured product composition (calc.) Amount of segments, % "H"	"S"	"Linking"	Physical properties of cured film[b] Tensile strength kg/cm²	Elastic modulus kg/cm²	Elongation %	Gel swell wt. %	First order diffraction efficiency Before heating	After heating	Change upon heating
1	0	35.8	43.0	21.2	340	8900	42	116	27.2%	26.7%	−1.8%
2	20	28.6	34.4	37.0	320	7000	51	88	27.6	27.2	−1.5
3	30	55.1	30.1	14.8	520	14300	21	122	25.5	25.1	−1.6
4	50	17.9	21.5	60.6	250	6500	53	142	25.9	25.1	−3.1
5	60	14.3	17.2	68.5	230	5900	46	177	27.6	24.7	−10.5
6	70	10.7	12.8	76.5	220	4100	70	171	26.3	23.8	−9.5

(a) The diluent monomer in all examples was 2-(N-butylcarbamyl)ethyl methacrylate, except in Example 3, where it was methyl methacrylate.

(b) These properties were measured in accordance with ASTM D 1708, using a crosshead speed of 12-in/min. (30-cm/min).

(c) The dynamnic shear moduli for the cured product of Example 2 were measured according to the procedure described in U.S. Patent 3,853,595 (Pedginski et al); the moduli were 5.7 x 10^8, 4.6 x 10^8, 3.2 x 10^8, 1.9 x 10^8, 4 x 10^7, 1.5 x 10^7, and 1.5 x 10^7 dynes/cm² at 23°, 50°, 60°, 70°, 80°, 100° and 120°C, respectively. The plot of these data on semi-logarithm graph paper falls within the area bounded by A—B—C—D of FIGURE 1.

The data of TABLE III show that dimensional stability (as manifested by the change in diffraction efficiency on heating) in the replicated articles is dependent on the amount of diluent monomer used due to its effects on the amount of different types of segments and on the crosslink density. Though the "H"/"S" ratios in these examples all were 0.83 (except in Example 3, where the ratio was 1.83), as the amount of "linking" segments and the molecular weight (MW) between crosslinks increased, the replicated articles had less dimensional stability. Thus, where a particular dimensional stability value is desired, for this particular plastic system, a particular amount of diluent monomer should be used, too much diluent monomer resulting in poor dimensional stability; for example, when 80% diluent monomer was used, the replicated article stuck to the mold because the shrinkage occurring upon curing caused the microstructure to mechanically "lock" onto the mold surface. For some applications of this system, for example a Fresnel lens to be used indoors at ambient temperature, a loss of dimensional stability of the magnitude shown in Examples 5 and 6 might be in acceptable limits, but for other applications, such as cube corner retroreflective sheeting, such losses will be unacceptable and the plastics of Examples 1—3 would be used.

EXAMPLE 7

Using the equipment of Example 1, there were added to the reactor 572.4 g (1.06 moles) polycarprolactone triol ("NIAX" PCP 0300), 334.8 g (1.56 moles) 2-(N-butyl-carbamyl)-ethyl methacrylate as a diluent monomer, 573.3 g (4.41 moles) 2-hydroxyethyl methacrylate, and 0.38 g dibutyltin dilaurate, and the contents of the reactor were mixed at 60°C until homogeneous. Then there was added 900 g (3.43 moles) of methylene bis(4-cyclohexylisocyanate) ("Hylene" WS) over a two-hour period with precaution taken to maintain the temperature below about 75°C. After the addition was complete, the resulting mixture was allowed to react further for 12 hours at 70°C, at the end of which time inspection of the infrared spectra of withdrawn samples of the resulting product showed it did not contain isocyanate, indicating complete reaction. Infrared analysis verified that the resulting oligomer product comprised acrylate-capped, polyester urethane oligomer (excluding the diluent monomer) having essentially the structure of formula XXX. The oligomer product had a calculated composition of 37.8 % "H" segments, 24.0% "S" segments, and 38.2% linking groups.

The oligomer product was diluted with 334.8 g (1.56 moles) 2-(N-butylcarbamyl)ethyl methacrylate to provide a 70% solution of the oligomer product for preparation of cured film and diffraction grating test samples, the composition and properties of which are set forth in TABLE IV.

EXAMPLE 8

Into a 1-liter metal reactor, equipped as described in Example 1, were charged 200 g (0.083 mole) poly(dimethylsiloxane)triol silicone fluid ("Dow Corning" Q4-3557), 210 g (1.60 moles) 2-hydroxyethyl methacrylate, and 0.3 g of dibutyltin dilaurate. The mixture was heated to 65°C and 220 g (0.99 mole) isophorone diisocyanate ("IPDI") was added over a two-hour period. The reaction was complete in 16 hours as determined by infrared analysis for isocyanate. The resulting acrylate-capped polysiloxane urethane oligomer product had a structure essentially that of formula XXI. Eighty parts of the oligomer product was diluted with 20 parts 2-(N-butylcarbamyl)ethyl methacrylate diluent monomer and the diluted oligomer product was cured to form film and diffraction grating test samples, the properties of which are set forth in TABLE IV.

EXAMPLE 9

Into a 1-liter reactor, equipped as described in Example 1, were charged 142 g (0.64 mole) isophorone diisocyanate ("IPDI") and 0.1 g of dibutyltin dilaurate. Next, 200 g (0.32 mole) polyoxytetramethylene diol ("Polymeg" 630, having a weight average molecular weight of 600) was added slowly over a 30-minute period; the temperature was kept below about 80°C during the addition. After a two-hour reaction period at a temperature of 75°C, 88.8 g (0.68 mole) 2-hydroxyethyl methacrylate was added to the resulting isocyanate-terminated urethane prepolymer product and the mixture allowed to react for 12 hours until inspection of the infrared spectra of the resulting oligomer

product indicated that complete reaction of isocyanate had occurred. As verified by infrared analysis, the acrylate-capped polyether urethane oligomer product had essentially the structure of formula XVIII

Eighty parts of the oligomer product was diluted with 20 parts 2-(N-butylcarbamyl)ethyl methacrylate diluent monomer and the diluted oligomer product was cured to form film and diffraction grating test samples, the compositions and properties of which are set forth in TABLE IV.

EXAMPLE 10

Into a 1-liter reactor at room temperature (25°C) were charged 224 g (1.10 moles) isophorone diisocyanate ("IPDI") and 0.3 g of dibutyltin dilaurate, and then over a period of about 45 minutes there was added a mixture of 312.5 g (0.25 mole) polycaprolactone diol ("NIAX" PCP 0230) and 27 g (0.3 mole) 1,4-butanediol chain extender, and the resulting reaction mixture allowed to rise to 80°C without application of external heat. After one hour, to the resulting isocyanate-terminated, chain-extended urethane prepolymer product, there was added 151.3 g (1.15 moles) 2-hydroxyethyl methacrylate and the mixture maintained at 75°C for 9 hours. The resulting acrylate-capped, chain-extended, polycaprolactone urethane oligomer product had essentially the structure of formula XXIII.

Eighty parts of the oligomer product was diluted with 20 parts 2-(N-butylcarbamyl)ethyl methacrylate, and the diluted oligomer product was cured to form film and diffraction grating test samples, the composition and properties of which are set forth in TABLE IV.

EXAMPLE 11

Into a 1-liter reactor, equipped as described in Example 1, was charged 157 g (0.60 mole) methylenebis-(4-cyclohexylisocyanate) ("Hylene" WS). Then, while stirring, there were added, over a period of one hour, a mixture of 288 g (0.12 mole) poly(dimethylsiloxane)diol silicone fluid ("Dow Corning" Q4-3667) and 1.83 g (0.03 mole) 2-aminoethanol chain-extender, and the temperature of the resulting mixture was allowed to rise to 70°C. The reaction was allowed to proceed for an additional hour at which time 131 g (1.00 mole) 2-hydroxyethyl methacrylate was added to the resulting isocyanate-terminate, chain-extended, urea-urethane prepolymer product. The mixture was held at 70°C and the reaction was complete in 12 hours as determined by infrared analysis, whereupon 248 g (1.08 moles) 2-(N-butylcarbamyl)ethyl methacrylate diluent monomer was added. Infrared analysis verified that the resulting acrylate-capped, chain-extended, polycaprolactone urea-urethane oligomer product (excluding the diluent monomer) had essentially the structure of formula XXXIII. Cured film and diffraction grating test samples were prepared and their compositions and properties are set forth in TABLE IV.

EXAMPLE 12

Into a 1-liter reaction vessel, equipped as in Example 1, were charged 120 g (0.46 mole) methylenebis-(4-cyclohexylisocyanate) ("Hylene" WS) and 0.25 g of dibutyltin dilaurate, and the mixture heated to 65—70°C while stirring. There was then added over a period of one hour a mixture of 219 g (0.091 mole) poly(dimethyl-siloxane)diol silicone fluid ("Dow Corning" Q4—3667) and 46 g (0.023 mole) poly(oxypropylene) diamine ("Jeffamine" D-2000) and the resulting mixture heated with stirring for an additional hour at 70°C. To the stirring mixture containing the resulting isocyanate-terminated, polysiloxane-polyether, urea-urethane prepolymer product was added 131 g (1 mole) 2-hydroxyethyl methacrylate and the resulting mixture was heated for three hours whereupon it was found by infrared analysis that all the isocyanate therein had disappeared. As verified by infrared analysis, the resulting acrylate-capped, polysiloxane-polyether, urea-urethane oligomer product had essentially the structure of formula XXXII.

Films and diffraction grating test samples were prepared using 70 parts of the above oligomer product diluted with 30 parts 2-(N-butylcarbamyl)ethyl methacrylate, the compositions and properties of these articles being set forth in TABLE IV.

EXAMPLE 13

Into a 1-liter reaction flask, equipped as in Example 1, were charged 250 g (0.95 mole) methylenebis-(4-cyclohexylisocyanate) ("Hylene" WS), 180 g (0.84 mole) 2-(N-butylcarbamyl)ethyl methacrylate, and 0.5 g of dibutyltin dialurate. The mixture was heated to 50°C and a mixture of 6.1 g (0.1 mole) 2-aminoethanol and 322 g (0.388 mole) of polycaprolactonediol (NIAX PCP 0210) was added over a one hour period. Then 131 g (1.0 mole) 2-hydroxyethyl methacrylate diluent monomer was added and heating at 50°C continued for 12 hours, at the end of which time it was confirmed by infrared analysis that isocyanate had disappeared. As verified by infrared analysis, the resulting oligomer product (excluding the diluent monomer) was an acrylate-capped, polycaprolactone, chain-extended, urea-urethane oligomer having essentially the structure of formula XXXIV.

Eighty parts of the oligomer product was diluted with 20 parts 2-(N-butylcarbamyl)ethyl methacrylate for the preparation of film and diffraction grating test samples, the compositions and properties of which are set forth in TABLE IV.

EXAMPLE 14

In a 4-liter reactor, equipped as in Example 1, a mixture of 15.1 g (0.13 mole) 1,6-hexamethylenediamine and 1250 g (0.52 mole) poly(dimethylsiloxane)diol silicone fluid ("Dow Corning" Q4-3667) was added during a one-hour period to a mixture of 572 g (2.58 mole) isophorone diisocyanate ("IPDI") and 2 g of dibutyltin dilaurate while maintaining the temperature of the reactor contents at 65—70°C. The mixture was heated at this temperature for an additional two hours to obtain the isocyanate-terminated polysiloxane, urea-urethane prepolymer product, and 536 g (2.76 moles) 2-hydroxyethyl methacrylate was then added over a one hour period. The resulting mixture was allowed to react at 65—70°C until the disappearance of isocyanate, as determined by infrared analysis, was observed, the period of reaction so required being 48 hours. Infrared analysis verified that the resulting acrylate-capped, polyester, urea-urethane oligomer product had essentially the structure of formula XXIV. The mixture was cooled, 593 g (2.57 moles) 2-N-butylcarbamyl)ethyl methacrylate diluent monomer was added, and film and diffraction grating test samples were prepared from the diluted oligomer product, the compositions and properties of these articles being set forth in TABLE IV.

EXAMPLES 15A and 15B

In a first run (Example 15A), into a 1.5-liter reaction flask, equipped as in Example 1, were placed 260 g (0.99 mole) methylenebis (4-cyclohexylisocyanate) ("Hylene" WS) and 0.1 g dibutyltin dilaurate. The mixture was heated to 65—70°C and 463.2 g (0.55 mole) polycaprolactonediol ("NIAX" PCP 0210) was added over a period of 1.3 hours. Isocyanate equivalent weight of the resulting reaction mixture was then monitored by butylamine titration as the reaction proceeded. When the isocyanate equivalent weight reached 798, indicative of complete reaction of the diol to produce the desired isocyanate-terminated, polycaprolactone, urethane prepolymer product, addition of 2-hydroxyethyl methacrylate was initiated. During 15 minutes, there was added 143 g (1.10 mole) of the methacrylate, taking care that the temperature did not rise above 75°C. After the addition, heating was continued until infrared analysis indicated that isocyanate had disappeared (14 hours). Infrared analysis verified that the oligomer product was an acrylate-capped, polyester urethane oligomer having essentially the structure of formula XXXI. In a second run (Example 15B), 534 g of isophorone diisocyanate ("IPDI"), 0.5 g dibutyltin dilaurate, 1000 g polycaprolactone diol ("NIAX" PCP 0210), and 300 g 2-hydroxyethyl methacrylate were reacted in the same manner as the first run to produce an oligomer product having the same structure as formula XVII except the number of repeating caprolactone ester units was 3.25 av. rather than 1.86 av. The oligomer products were diluted with 20 percent by weight of 2-(N-butylcarbamyl)ethyl methacrylate for preparation of film and diffraction grating test samples, the compositions and properties of which are set forth in TABLE IV.

EXAMPLE 16

Into a 1-liter reaction flask, equipped as in Example 1, were placed 88.8 g (0.4 mole) isophorone diisocyanate ("IPDI") and 0.2 g dibutyltin dilaurate. The mixture was heated to 70°C and 250 g (0.2 mole) polycaprolactonediol ("NIAX" PCP 0230) was added during 40 minutes while maintaining the temperature of the reactor contents at 70—75°C. The mixture was held at this temperature for three hours, resulting in an isocyanate-terminated, polycaprolactone urethane prepolymer. There was then added 55 g (0.45 mole) 2-hydroxyethyl methacrylate and heating was continued at 75°C for 15 hours. At the end of this time, infrared analysis indicated that the isocyanate group had disappeared. As verified by infrared analysis, the acrylate-capped, polycaprolactone, urethane oligomer had essentially the structure of formula XIX. The oligomer product was diluted with 20 percent by weight of 2-(N-butylcarbamyl) ethyl methacrylate and film and diffraction grating test samples were prepared from the diluted product, the compositions and properties of these articles being set forth in TABLE IV.

EXAMPLE 17

Example 1 was repeated except that the polycaprolactonediol used was "NIAX" PCP 0240. The resulting acrylate-capped, polycaprolactone urethane oligomer had the same structure as that shown by formula XIX, but the number of repeating units in the polyester segment was 8.4 (AV.) The oligomer product obtained was diluted with 20 percent by weight of 2-(N-butylcarbamyl)ethyl methacrylate for preparation of films and diffraction grating test samples, the compositions and properties of these articles being set forth in TABLE IV.

The data of TABLE IV show that though the "H"/"S" ratios varied from 0.22/1 to 1.57/1 and the physical properties (viz., tensile, modulus, elongation) varied widely, the dimensional stability of the articles (made from a host of different resin systems) varied only over a relatively narrow range of acceptable values, though, here again, the desired dimensional stability of an application might require use of one system rather than another. The optical properties shown for these systems will also dictate the particular applications to be made, for example, a lens application would require high transmission, e.g. greater than 91% and low haze, e.g., less than 5%, whereas a retroreflective video disc could tolerate lower transmission and higher haze.

TABLE IV

Ex.	Cured product compositon (calc) Amount of Segments, % "S"	"H"	"Linking"	Physical properties of cured film [a] Tensile strength kg/cm²	Elastic modulus kg/cm²	Elongation %	Gel swell wt. %	First order diffraction efficiency Before heating	After heating	Change upon heating	Optical Properties[b] Transmission %	Haze %
7	21.1	33.1	45.8	600	11700	14	80	27.6%	26.7%	—3.1%	92.4	0.9
8	25.4	27.9	46.7	240	4600	9	76	27.6	25.8	—6.5	91.2	1.4
9	37.1	26.4	36.6	220	2000	74	91	27.6	28.4	+3.1	92.4	0.9
10	35.0	28.1	36.9	310	6800	48	119	26.7	26.7	0	91.2	1.3
11	34.9	19.2	45.9	170	3200	24	—	26.3	25.9	—1.6	91.9	1.8
12	36.0	16.3	47.7	160	2900	51	81	25.5	25.4	—0.3	91.8	3.4
13	29.0	23.0	48.0	300	6400	87.5	103	27.2	26.8	—1.6	92.2	4.7
14	42.1	19.8	38.1	150	2300	28	85	23.8	23.8	0	90.1	8.2
15	42.3	24.3	33.4	220	2200	60	106	25.5	25.1	—1.7	92.4	1.1
15A	43.6	23.3	33.1	170	600	95	90	27.6	25.8	—6.6	92.5	0.7
16	50.8	18.0	31.2	140	450	146	121	25.9	23.4	—9.8	92.1	1.3
17	58.8	13.0	28.2	100	340	168	153	21.3	19.2	—9.8	91.4	2.4

(a) These properties were determined according to ASTM D 1708, using a crosshead speed of 12-in/min (30-cm/min).
(b) These properties were determined according to ASTM D 1003.

Portions of the films of Examples 7, 9, 13 and 15 were used to measure their dynamic shear moduli according to the procedure of U.S. Patent 3,853,595; these measurements were plotted on semilogarithm paper, and values from the plotted curves at particular temperatures are set forth in TABLE V, said plotted curves falling within the area A—B—C—D of FIG. I.

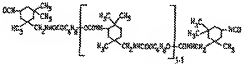
TABLE V

Dynamic shear modulus, dynes/cm²

Temperature °C	EXAMPLES 7	9	13	15A	15B
23	3.7×10^9	2.3×10^9	1.9×10^9	1.4×10^9	2.0×10^8
40	3.2×10^9	1.3×10^9	1.4×10^9	1.1×10^9	1.2×10^8
50	2.7×10^9	0.8×10^9	0.9×10^9	0.9×10^9	3.0×10^7
60	2.0×10^9	2.5×10^8	1.7×10^8	0.5×10^9	1.4×10^7
70	1.4×10^9	1.1×10^8	7.2×10^7	1.5×10^8	1.0×10^7
80	1×10^9	6.6×10^7	6.1×10^7	7.5×10^7	8.0×10^6
100	1.8×10^8	4.2×10^7	3.3×10^7	4.2×10^7	6.9×10^6
120	9.2×10^7	4.0×10^7	3.0×10^7	3.4×10^7	6.5×10^6

EXAMPLE 18

To a 500-ml glass reaction vessel, equipped as in EXAMPLE 1, were added 200 g (0.91 mole) isophorone diisocyanate ("IPDI"), 6 drops of dibutyltin dilaurate catalyst, and 80 g (0.35 mole) 2-(N-butylcarbamyl)ethyl methacrylate. While maintaining thorough mixing of the reactor contents, 60 g (0.67 mole) 1,4-butanediol was added slowly and the temperature was kept below about 80°C. The polymerization was allowed to proceed for 2.3 hours, at which time the isocyanate equivalent weight was found to be at 863, indicating a complete reaction to form an isocyanate-terminated, chain-extend urethane prepolymer product containing a block of the following structure:



(XXV)

To the above-prepared prepolymer product, 89 g (0.107 mole) polycaprolactone diol ("NIAX" PCP 0210) was added and allowed to react for 2 hours. This was followed by 309 g (0.235 mole) 2-hydroxyethyl methacrylate. The resulting reaction was complete, as determined by infrared analysis, in an additional 11 hours. The resulting acrylate-capped, polycaprolactone, chain-extended urethane bloc oligomer product was calculated as containing 56.5% urethane "H" segments and 19.3% polycaprolactone "S" segments. Infrared analysis of the oligomer product confirmed it had essentially the structure of formula XXV.

Fifty parts of the above-prepared oligomer product was dissolved in 50 parts tetrahydrofuran solvent, and 1.0 part of 2,2-diethoxyacetophenone was added to the mixture and the resulting composition was used to make a replicated diffraction grating by the procedure described hereinbefore

during the preparation of the grating, the solvent was allowed to evaporate from the solution, leaving the oligomer layer on the master molding surface. The dimensional stability of the subsequently radiation-cured grating was determined by the aforesaid procedure and found to be acceptable as shown by the following data:

First order diffraction efficiency		
Before heating	After heating	Change
24.7%	23.0%	−6.9%

EXAMPLE 19

Eighty g (0.235 mole) of the diglycidyl ether of bis-phenol A ("DER" 322) was combined with 20 g (0.024 mole) polycarolactone diol ("NIAX" PCP 0210), 2 g of the phosphorous hexafluoride salt of the diphenyl iodonium cation (as a photoinitiator), and 0.5 g of 2-chloro thioxanthone (as a photosensitizer). A diffraction grating was prepared from the resulting mixture by the procedure described hereinbefore, the cured polymer containing 63% "H" segments, 20% "S" segment units. The in situ formed oligomer had essentially the structure shown by formula LII. The dimensional stability of the diffraction grating was tested by the aforesaid procedure and found to be acceptable, as shown by the following data:

First order diffraction efficiency		
Before heating	After heating	Change
26.8%	25.5%	−4.85%

The gel swell of the crosslinked polymer was 40%.

EXAMPLE 20

To 70 parts of diluted oligomer prepared as described in Example 7 (which was a mixture of 88 parts oligomer and 30 parts of 2-(N-butylcarbamyl)ethyl methacrylate) were added 30 further parts of the latter methacrylate and 0.7 part 2,2-diethoxyacetophenone. The resulting mixture was mixed thoroughly and vacuum degassed to remove air bubbles. The resulting curable mixture was poured onto a rectangular (20 cm x 30 cm) metal mold master of electroformed nickel whose molding surface was in the form of an array of about 50,000/inch^2 (7800/cm^2) negative or female cube corner depressions or cavities 0.128 mm in depth, each edge of each cube corner being 0.0045 inch (0.116 cm) in length. The resulting layer of the curable mixture was covered with a 3 mil (0.077 mm) thick film of polyethylene terephthalate polyester. The resulting construction was placed in a 2 ton (1910 kg) platen press and heated under pressure to 70°C, this operation forcing the curable mixture into the cube corner depressions and forcing out air bubbles. The construction was then subjected to radiation curing using an ultraviolet radiation processing unit ("QC Processor", made by Radiation Polymer Corp.) in the same manner as that used in preparing the diffraction grating test samples described above. A total of 10 passes of the construction in a nitrogen atmosphere at a conveyor speed of 80 ft/min. (24.5 m/min.) was used in the curing operation. The resulting cured sheeting of the replicated array of cube corners, having an overall thickness of about 10 mils (0.25 mm), was removed from the mold and then square pieces, 9 inches^2 (58 cm^2), were cut from the sheet as test specimens. Each test specimen was mounted on an aluminium panel (by adhering the edge portions of the specimen to the panel with pressure sensitive adhesive tape), with the cube corner elements in contact at their apices with the panel and with air pockets between the cube corner elements trapped between the specimen and panel, thus forming a retroreflective article based on a form depicted in FIGS. 3, 4.

One of the above prepared articles was tested for retroreflectivity by placing it in a darkroom at a distance of 50 feet (15 m) from a light source mounted in a plane normal to the plane of the article, the exposed flat surface of the array of cube-corners of which faced the light source. A photodetector was positioned at a small angle ("divergence angle") relative to the plane normal to the article and the brightness of the article upon illumination of the light source was measured (in accordance with test procedure 4.7.7.2 of U.S. Federal Specification L-S-300B, July 12, 1974), at the customary divergence angle of 0.2°. Following these measurements, the article was heated at 110°C in an air oven for 120 hours, cooled to ambient room temperature, and its brightness was measured again. The other of the above-prepared articles were coated with a methyl ethyl ketone solution of acrylic topcoat (sold as XP903 by Rohm & Haas Co.) containing 0.5 wt.% "UVINUL"-539 acrylate UV-absorber, and the coating dried to provide a 0.01 mm thick layer. Then, the so-coated article was placed in an XW Weatherometer and exposed thereto to temperatures up to 45°C, intense ultraviolet light, and relative humidity of 90% and higher, the article being withdrawn periodically, tested for brightness determination, and reinserted.

The other coated article was subjected to prevailing weather condition in the state of Florida for 1 year and the brightness measured after such exposure. The results of the brightness tests are as follows:

	Brightness, candles/lumen at 0.2° divergence angle
Uncoated article	
Before heating	1630
After heating	1120
Coated article	
Exposed in XW Weatheromer after	
0 hours	1373
100 hours	1108
500 hours	847
1000 hours	950
1500 hours	855
Florida article	
Before exposure	931
After 1 year exposure	402

The above data show that the various articles had high brightness, particularly in comparison with commercial varieties of glass-beaded retroreflective sheeting, for example as taught in U.S. Pat. No. 2,407,680, which typically exhibit a brightness of 30 candles/lumen. The relatively small changes in the brightness of the articles show the dimension stability of the cured plastic.

EXAMPLE 21

One hundred kilograms of oligomer product prepared as described in Example 15A was diluted with 30% by weight 2-hydroxyethyl methacrylate. One percent by weight of a benzoin ether photoinitiator (sold under the trademark "VICURE" 30) was added and blended thoroughly with the diluted oligomer product. The resulting curable mixture was then used to make in a continuous process a continuous sheet (33 cm in width) of contiguous, replicated, linear Fresnel lens elements (ca. 30 cm x 30 cm), like that of FIG. 6 using the equipment schematically shown in FIG. 9.

In this operation, a stream of the curable mixture was supplied from source container 31, to a metering pump 32 which passed the curable mixture to extrusion die 33. The curable mixture was extruded onto a metal master roll 34 of electroformed nickel, containing on its surface linear Fresnel lens elements pattern 35 having a line frequency of 100 lines/inch (39.5 lines/cm). a cover film 36 of polyethylene terephthalate polyester, passing over rolls 37 and 38 and drawn by windup roll 39, was applied to the top of the layer 41 of curable mixture on the lens pattern 35 and the resulting covered layer passed by a bank of medium pressure mercury arc lamps 42 (made by Radiation Polymer Corp.) at a rate of 10 ft/min. (3.1 m/min.) and the resulting laminate 43 comprising the contiguous replicated Fresnel lenses was wound as a roll on the windup roll 39. The laminate 43 was removed from the windup roll 39, the polyester sheet stripped from the lens elements, and individual Fresnel lens elements cut therefrom. A focusing array of four such lens elements was mounted in a package and the latter was inserted as a Fresnel lens onto an overhead projector (Model No. 213, manufactured by the 3M Company) and its image projecting quality evaluated by projecting the image from a transparency (containing a variable frequency target pattern) onto a projection screen at a magnification of about 6X. The resolving power on the screen was found to be excellent, as viewed by the unaided eye at normal

viewing distances.

EXAMPLE 22

A metal video disc master prepared in a manner like that described in "Optics & Laser Technology", supra, was mounted in a mold cavity designed to hold the master flat. The master contained information (viz., a full-color, 30-minute, sound movie) in the form of 1.5 micron long, 0.75 micron wide, and 0.3 micron high raised areas arranged in radial tracks spaced about 1.5 microns apart. A vacuum degassed sample of the oligomer product of Example 5 (diluted with 30% by weight 2-hydroxyethyl methacrylate and containing 0.75% 2,2-diethoxyacetophenone) was injected by a syringe into the mold, which was covered by an optically ground, smooth glass plate 1/2 inch (0.127 cm) in thickness, leaving a mold cavity 10 mil (0.254 mm) in depth between the master molding surface and the glass plate. The construction was exposed to ultraviolet radiation using the processing equipment used to cure the above-described diffraction grating samples. The resulting replicated video disc, schematically shown in FIGS. 7 and 8, was removed from the mold and it exhibited to the unaided eye under visible light a diffracted light pattern like that of the video disc master. The information-bearing surface of the replicated video disc was vapor coated with a thin layer (about 2000 A in thickness) of aluminum to permit reading of the disc by reflection. Readout of the information was accomplished by playing the disc on a laser beam player, such as that described in "Spectrum", January, 1975, p. 67.

The reproduction of the movie film was of excellent quality with a high-signal-to-noise ratio. Examination of the replicated video disc with an optimal microscope revealed that the disc had a total eccentricity (or "out-of-roundness") of less than 0.5 mil (0.013 mm), attesting to the outstanding dimentional stability of the replication. The video disc was also inverted with the information on the down-side and played on said laser beam player, the laser beam being transmitted through the plastic interior of the disc to the information bearing surface (where modulation occurs), and then reflected back through the plastic interior to the photodiode of the player. In this inverted mode, the reproduction of the movie film was again found to be excellent, attesting to the optical homogenity (viz., freedom from birefringence) of the plastic.

EXAMPLE 23

The oligomeric composition of Example 7 was also used to make a diffraction grating test sample which was cured with an electron beam processor (sold under the trademark "Electrocurtain"), using a 12-inch (30 cm) wide electron beam, a dosage of 5×10^6 rads, and a nitrogen atmosphere. The first order diffraction efficiency of the sample was 22.5% before heating and 21% after heating (at 130°C for 1 hour), the change on heating being 6.6%.

Various modifications and alterations of this invention will become apparent to those skilled in the art without departing from the scope and spirit of this invention.

CLAIMS

1. An article comprising a shaped, plastic, monolithic layer having a microstructure-bearing surface and comprising crosslinked polymer composed of (1) a plurality of hard segments of mono- or polyvalent moieties containing one or more carbocyclic and/or heterocyclic groups, and (2) a plurality of soft segments of mono- or polyvalent moieties.

2. An article according to claim 1 wherein each of said moieties of said hard segments, when their valences are satisfied by protons, has at least one major transition temperature above 250°K, and wherein each of said moieties of said soft segments has a number average molecular weight of about 500 to 5000 and homopolymers thereof have a glass transition temperature below 250°K.

3. An article according to claim 1 wherein said crosslinked polymer has a gel swell within the range of 35 to 200 weight percent.

4. An article according to claim 1 wherein said crosslinked polymer has 10 to 80 weight percent of said hard segments and 10 to 60 weight percent of said soft segments.

5. An article according to claim 1 wherein said crosslinked polymer has dynamic shear moduli, over the temperature range of 23°C to 120°C, which fall on or within the boundary of A—B—C—D of FIG. 1.

6. An article according to claim 1 wherein a diffraction grating of said crosslinked polymer has a first order diffraction efficiency which changes less than 15% when heated at 130°C for 1 hour as compared to the first order diffraction efficiency before heating.

7. An article according to claim 1 wherein said microstructure-bearing surface has an average profile which is piano, convex, concave, aspheric, or combinations thereof, said surface having discontinuities whose heights deviate from said average profile by $\pm 0.005\ \mu m$ to $\pm 750\ \mu m$, said surfaces being free of utilitarian discontinuities or having one or a plurality of utilitarian discontinuities which are the same or different and spaced apart or contiguous in a random or ordered manner.

8. An article according to claim 7 wherein said microstructure-bearing surface is free of utilitarian discontinuities.

9. A shaped plastic article comprising a shaped, plastic, monolithic layer having a replicated microstructure-bearing surface and comprising crosslinked polymer composed of (1) a plurality of hard

segments of mono- or polyvalent moieties containing one or more carbocyclic and/or heterocyclic groups and difunctional linking groups with hydrogen bonding capability, and (2) a plurality of soft segments of mono- or polyvalent moieties, wherein each of said moieties of said hard segments, when their valences are satisfied by protons, has at least one major transition temperature above 250°K, and wherein each of said moieties of said soft segments has a number average molecular weight of about 500 to 2500 and homopolymers thereof have a glass transition temperature below 250°K, said crosslinked polymer having a gel swell within the range of 35 to 200 weight percent, 10 to 80 weight percent of said hard segments and 10 to 60 weight percent of said soft segments, and dynamic shear moduli, over the temperature range of 23°C to 120°C, which fall on or within the boundary of A—B—C—D of FIG. 1, and wherein a diffraction grating of said crosslinked polymer has a first order diffraction efficiency which changes less than 15% when heated to 130°C for 1 hour as compared to the first order diffraction efficiency before heating.

10. An article according to claim 1 in the form of a Fresnel or echelon lens element or a retroreflective sheet comprising an array of cube-corner prism elements.

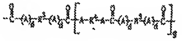
11. An article according to claim 1 wherein said crosslinked polymer is formed upon radiation of an oligomeric composition comprising one or more oligomers having (1) one or more like or different hard segments each comprising a mono- or poly-valent moiety containing one or more carbocyclic and/or heterocyclic groups, (2) one or more like or different soft segments each comprising a mono- or poly-valent moiety selected from the group consisting of polyester, polysiloxane, polyacrylate, polyether and polyolefin, and (3) one or more like or different monovalent moieties containing a radiation sensitive, addition-polymerizable, functional group selected from the group consisting of acrylyl, methacrylyl, allyl, and vicepoxy.

12. An article according to claim 1 in the form of a video disc.

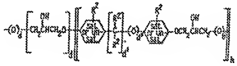
13. An article according to claim 1 in the form of a diffraction grating.

14. An article according to claim 1 in the form of an ophthalmic lens.

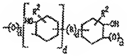
15. An article according to claim 1, wherein said hard segments are represented by one or more of the following formulas:



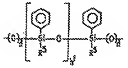
V



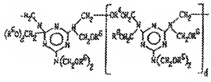
VI



VII

and 

VIII



IX

where
each A is independently —NH— or —O—,
each B is

$$-(CH_2)_f-,\ -CO-,\ -(CH_2-CO)- \text{ or}$$

$$-(CH_2)_f-OC(O)-(CH_2)_f-C(O)O(CH_2)_f-,$$

where f is an integer of 2 to 5,
each R^2 is independently hydrogen or a lower alkyl,
each R^3 is independently a di-valent carbocyclic-containing radical derived from benzene, naphthalene, cyclohexane, dicyclohexylmethane, diphenylmethane or norbornene, and their lower alkyl-substituted derivatives, by removal of two of their hydrogen atoms,
each R^4 is independently an alkylene moiety with 2 to 10 carbon atoms, or a cycloalkylene moiety with 6 to 10 carbon atoms,
each R^5 is independently a phenyl moiety or methyl
each R^6 is independently a lower alkyl with 1 to 4 carbon atoms,
g is zero or a number up to 5,
h is an integer of 1 to 10
h' is zero or an integer of 1 to 10,
each d,d' and d" is independently zero or 1, with the proviso that if either one of d' or d" is 1, then the other is zero,

and wherein said soft segments are residues remaining from removal of the active hydrogen atoms of one or more of the following: poly(oxyalkylene) polyols, polyester polyols, polyether polyester polyols, polyolefin polyols, polysiloxane polyols, poly(alkylacrylate) polyols, and polyamines.

16. An article according to claim 15 wherein said soft segments are represented by one or more of the following formulas:

$$-\left[A-R^7-(OR^7)_i-O\right]_j-(R^8)_d\,(R^7-A)_c \qquad \text{I}$$

where each A is independently —NH— or —O—,
$(OR^7)_i$ is oxyalkylene or poly(oxyalkylene),
R^7 is an alkylene of 2 to 4 carbon atoms, such as

$$-(CH_2)_2-,\ -(CH_2)_3-,\ -(CH_2)_4-,\ -CH_2CH(CH_3)-,$$

$$-CH_2CH(CH_3)CH_2-, \text{ and } -CH(CH_3)CH(CH_3)-,$$

R^8 is a saturated aliphatic radical free of active hydrogen atoms and which can contain 1 or 2 non-vicinal catenary oxygen or nitrogen atoms, R^8 having a valence equal to j and 2 to 10 carbon atoms,
i is a number of 1 to 20,
j is an integer of 1 to 3, and
d and c are each independently zero or 1 with the provisos that when d is 1, then c is zero and j is 2 or 3, and when d is zero, then j is 1,

$$\left[\left[\left[O-(CH_2)_{e'}\right]_p-O-(\overset{O}{\overset{\|}{C}})_a-(CH_2)_{e'}-\overset{O}{\overset{\|}{C}}-O\right]_r-\left[(CH_2)_{e'}-O\right]_o\right]_s(R^9)_q \qquad \text{II}$$

where R^9 is a saturated aliphatic radical free of active hydrogen atoms and can contain 1 or 2 non-vicinal catenary oxygen or nitrogen atoms, R^9 with a valence equal to s and 2 to 10 carbon atoms,
each a, o, p and q is independently zero or 1,
each e' is independently an integer of 2 to 10,
each r is independently a number of 1 to 20,
each s is independently an integer of 1 to 3 with proviso that

when q is 1, then s is 2 or 3 and o is zero and either a and p are both zero or both 1, and when q is zero, then s and o are 1 and either a and p are both zero or both 1,

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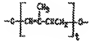
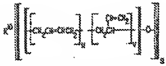
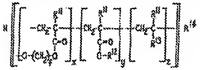
 XII

where t is a number of 7 to 35,

and  XIII.

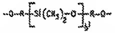
where the group enclosed by the single brackets with the subscripts u and v are repeating units randomly distributed within the double brackets and u and v are integers whose sum is from 2 to 20 and u/v is a ratio of 1/4 to 4/1, s is 2 or 3, and R^{10} is polyvalent carbocyclic-containing radical derived from benzene, naphthalene, or a phenyl-substituted benzene by removal of 2 or more hydrogen atoms,

 XIV

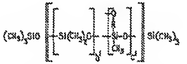
where each

R^{11} is independently hydrogen or methyl,
R^{12} is independently an alkyl of 2 to 10 carbon atoms, preferably butyl,
R^{13} is independently —$C(O)OCH_3$, —CN or phenyl,
R^{14} is —$SR^{15}H$, —$SR^{15}O$—, —$SCH_2C(O)OR^{15}H$ or H, where R^{15} is an alkylene having 1 to 12 preferably 2, carbon atoms,
f is an integer of 2 to 5

the groups enclosed by the single brackets with subscripts x, y and z are repeating units randomly distributed within the double brackets, the sum of x, y and z being such that the number average molecular weight of the totality of said repeating units is about 500 to 5000, the units enclosed by brackets with subscripts x and y always being present and the units enclosed by the bracket with subscript z being optionally present,
or "S" in formula I is a said polysiloxane residue represented by the formulas:

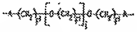
 XV

where b' is a number of 8 to 35, and R is a linear or branched alkylene group having 1 to 12 carbon atoms or a polyoxyalkylene group having 4 to 80 carbon atoms and 1 to 40 oxygen atoms,

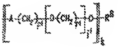
and  XVI

where the groups enclosed by the single brackets with subscripts 'b and c' are repeating units randomly distributed within the double bracket, b' being a number of 8 to 35 and c' being 2 or 3, and R is as defined above.

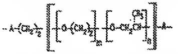
17. An article according to claim 16 wherein said soft segments are represented by one or more of the following formulas:

 XA

where preferably each f' is independently 3 to 5 (more preferably 4) and i' is 5 to 10,

 XB

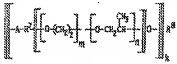
where l' is 3 to 5, i' is 5 to 10, and k is 2 or 3, and is the valence of R^8



XC

where the groups enclosed by the single brackets with subscripts m and n are repeating units randomly distributed, m is zero or 1 to 4, n is 4 to 20, with the proviso that n/m is at least 4,

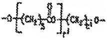
and



XD

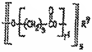
where the groups enclosed by the brackets with subscripts m and n are repeating units randomly distributed within the double brackets, m, n, and n/m are as defined above, and k is 2 or 3 and is the valence of R^8.

18. An article according to claim 16 wherein said soft segments are represented by one or more of the following formulas:



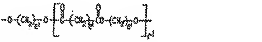
XIA

where r' is a number of 1 to 10 and s' is 2 or 3.



XIB

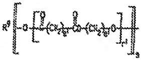
where r' is a number of 1 to 10 and s is 2 or 3, and R^9 is oxyalkylene, polyoxyalkylene, or alkanetriyl,



XIC

where each s' is independently a number of 2 to 5 and r' is a number of 1 to 10, and

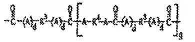
and



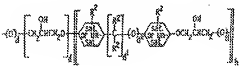
XID

where s' is a number of 2 to 5, r' is a number of 1 to 10, R^9 is as defined above, and s is 2 or 3.

19. An article according to claim 1 wherein said hard segments are represented by one of the following formulas:



V



VI

where
each A is independently —NH— or —O—,
each R^2 is independently hydrogen or a lower alkyl,
each R^3 is independently a di-valent carbocyclic-containing radical derived from benzene, naphthalene, cyclohexane, dicyclohexylmethane, diphenylmethane, or norbornene, and their lower alkyl-substituted derivatives, by removal of two of their hydrogen atoms,

each R^4 is independently an alkylene moiety with 2 to 10 carbon atoms, or a cycloalkylene moiety with 6 to 10 carbon atoms,
g is zero or a number up to 5,
h is an integer of 1 to 10
h' is zero or an integer of 1 to 10,
each d, d' and d'' is independently zero or 1, with the proviso that if either one of d' or d'' is 1, then the other is zero,
and said soft segments are represented by one of the following formulas:

$$-O\left[(CH_2)_5-\overset{O}{\overset{\|}{C}}O\right]_{r'}(CH_2)_{s'}O- \qquad \text{XIA}$$

where r' is a number of 1 to 10 and s' is 2 or 3.

$$\left[-O\left[(CH_2)_5-\overset{O}{\overset{\|}{C}}O\right]_{r'}\right]_s R^8 \qquad \text{XIB}$$

where r' is a number of 1 to 10 and s is 2 or 3, and R^8 is oxyalkylene, polyoxyalkylene, or alkanetriyl.

20. An article according to claim 1 wherein said hard segments are represented by the formula:

$$-\overset{O}{\overset{\|}{C}}-(A)_d-R^3-(A)_d-\overset{O}{\overset{\|}{C}}\left[A-R^4-A-\overset{O}{\overset{\|}{C}}-(A)_d-R^3-(A)_d-\overset{O}{\overset{\|}{C}}\right]_g \qquad \text{V}$$

where
each A is independently —NH— or —O—
each R^3 is independently a di-valent carbocyclic-containing radical derived from benzene, naphthalene, cyclohexane, dicyclohexylmethane, diphenylmethane, or norbornane, and their lower alkyl-substituted derivatives, by removal of two of their hydrogen atoms,
each R^4 is independently an alkylene moiety with 2 to 10 carbon atoms, or a cycloalkylene moiety with 6 to 10 carbon atoms,
g is zero or a number up to 5, and each d is independently zero or 1,
and said soft segments are represented by one of the following formulas:

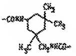
$$-O-R-\left[Si(CH_3)_2-O\right]_{b'}-R-O- \qquad \text{IX}$$

where b' is a number of 6 to 35, and R is a linear or branched alkylene group having 1 to 12 carbon atoms or a polyoxyalkylene group having 4 to 80 carbon atoms and 1 to 40 oxygen atoms,

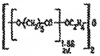
$$\text{and} \quad (CH_3)_3SiO\left[\left[-Si(CH_3)_2O-\right]_{b'}\left[-\underset{CH_3}{\overset{\overset{O}{|}\\R}{Si}}-O-\right]_{c'}\right]Si(CH_3)_3 \qquad \text{XII}$$

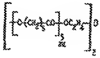
where the groups enclosed by the single brackets with subscripts 'b and c' are repeating units randomly distributed within the double bracket, b' being a number of 6 to 35 and c' being 2 or 3, and R is as defined above.

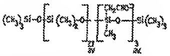
21. An article according to claim 1 wherein said hard segments comprise those represented by the formula



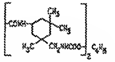
and said soft segments comprise those represented by one of the following formulas



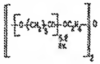




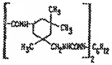
22. An article according to claim 1 wherein said hard segments comprise those represented by the formula:



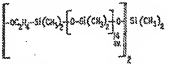
and said soft segments comprise those represented by the formula:



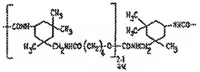
23. An article according to claim 1 wherein said hard segments comprise those represented by the formula:



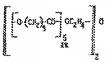
and said soft segments comprise those represented by the formula:



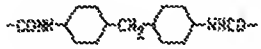
24. An article according to claim 1 wherein said hard segments comprise those represented by the formula:



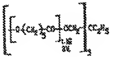
and said soft segments comprise those represented by the formula:

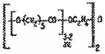


25. An article according to claim 1 wherein said hard segments comprise those represented by the formula:

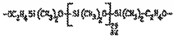


and said soft segments comprise those represented by one of the following formulas:

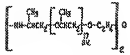




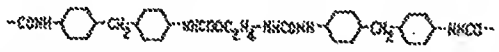
or said soft segments comprise those represented by the following two formulas:



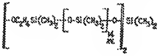
and

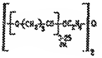


26. An article according to claim 1 wherein said hard segments comprise those represented by the formula:

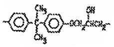


and said soft segments comprise that those represented by one of the following formulas:

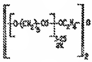




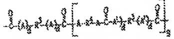
27. An article according to claim 1 wherein said hard segments comprise those represented by the formula:

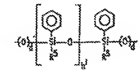


and said soft segments comprise those represented by the formula:



28. A plastic diffraction grating comprising a shaped, plastic, monolithic layer having a diffraction grating-bearing surface and comprising crosslinked polymer composed of (1) 20 to 50 weight percent of a plurality of hard segments selected from those represented by one or both of the formulas



and  VIII

where

each A is —NH— or —O—,

A' is —NH—,

each R^3 is independently a di-valent carbocyclic-containing radical derived from benzene, naphthalene cyclohexane, dicyclohexylmethane, or diphenylmethane, and their lower alkyl-substituted derivatives, by removal of two of their hydrogen atoms,

each R^4 is independently an alkylene moiety with 2 or 4 carbon atoms, or a cycloalkylene moiety with 6 to 10 carbon atoms,

each R^5 is phenyl,

each d is independently zero or 1

g is zero or a number having an average of 1 to 3, and

h' is zero or an integer of 1 to 10.